Geochemical characteristics and organic carbon sources within the upper reaches of the Xi River, southwest China during high flow

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Carbon (POC, DOC) and carbon isotopes ($\delta^{13}\text{C}$) within two headwater tributaries to the Xi River Basin, southwest China were analyzed to document the geochemical characteristics and sources of organic carbon (C) within basins characterized by a monsoonal climate and karst landforms. $\delta^{13}\text{C}_{\text{POC}}$ value and C/N ratio data indicate that suspended soil organic carbon (SOC) was an important source of POC in both the Nanpan and Beipan rivers (i.e., the studied tributaries). However, differences in C sources exist between the Nanpan and Beipan River Basins. Higher terrestrial plants supplied a portion of the POC within the Beipan River. In contrast, the Nanpan River was characterized by an inverse correlation between POC and DOC, and a positive relationship between the $\delta^{13}\text{C}$ values. These trends indicate that DOC within the Nanpan River was partly derived from the degradation of soil C within the water column. In addition, the interception of C by hydrological projects (e.g., dams) positioned along the Nanpan River led to higher DOC/POC ratios. In contrast, within the Beipan River $\delta^{13}\text{C}_{\text{DOC}}$ values range from -20 to -25.2‰ and are consistent with ratios associated with soil C, suggesting that leaching of C from catchment soil was the dominant source of DOC. Organic C in tributaries to the Beipan River may also have been derived from intense upland soil erosion, a process that resulted in the lowest DOC/POC ratios. The collected data indicate that land-use changes have potentially influenced regional- to local-scale organic C budgets within subtropical basins subjected to karstification.

1. Introduction

Lateral carbon (C) fluxes play a significant role in the global C cycle, including the linkages between terrestrial and marine C pools (Meybeck 1982; Ludwig *et al.* 1996; Beusen *et al.* 2005; Regnier *et al.* 2013; de Wit *et al.* 2015). Recent studies suggest that vertical C fluxes (1.8 Pg C yr^{-1}) released into the atmosphere are twice the lateral fluxes (0.9 Pg C yr^{-1}) to the ocean (Wehrli 2013). Therefore, quantitative studies that integrate both lateral and vertical C fluxes at regional to global scales are needed to predict feedbacks to climate change (Richey *et al.* 2002; Battin *et al.* 2009;

Raymond *et al.* 2013). At the local scale, organic C is a significant source of energy to riverine ecosystems (e.g., for aquatic biota) and closely influence acid buffering as well as the transport and availability of ions, nutrients, heavy metals and organic pollutants (Hope *et al.* 1994; Evans *et al.* 2005; Dawson *et al.* 2008). Therefore, the dynamics of dissolved organic C in streams and rivers serves as an important control on acidification processes, heterotrophic productivity, respiration, C cycling and short-term CO_2 outgassing (Vidon *et al.* 2014).

Spatial and temporal variations in major ion concentrations, the concentrations of various C species, and the isotopic composition of organic

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C can be deciphered to develop an understanding of the geochemical and biogeochemical factors that regulate various physio-chemical indexes (pH, T, DO, alkalinity, etc.) in riverine ecosystems. This is particularly true for monsoon-affected, subtropical basins such as those located in southwest China. Here, temporal variations in C concentrations and isotopic values may exist due to the enhanced erosion of soil from dry arable uplands close to the riverbanks during the monsoon season. Organic C from these upland soils are characterized by relatively high $\delta^{13}\text{C}$ values (Tao *et al.* 2009).

This paper uses C isotopic methods coupled with other geochemical parameters to investigate differences in the geochemical characteristics and sources of organic C within the Nanpan and Beipan rivers, two upstream tributaries to the Xi River.

2. Geographic, hydrologic, and geochemical setting

The Nanpan and Beipan rivers represent headwater tributaries to the Xi River. The Xi River ultimately forms the main channel of the Pearl River, the second largest river in China (only the Yangtze is larger). The Xi River basin is characterized by a mean annual temperature that ranges between 14 and 22°C, and a distinct dry-wet (monsoonal) climatic regime. Average annual rainfall ranges between a low of 800 mm during the dry winter

season and a high of 1200 mm during the summer months. Precipitation during the rainy period (June–September) accounts for about 80% of the total annual precipitation. The monsoonal climate results in large seasonal differences in estimated organic C fluxes to the ocean. In fact, organic C fluxes may vary by as much as 18 folds during a given year (Zhang *et al.* 2009). Variations are particularly pronounced for POC.

Both tributaries (i.e., the Nanpan and Beipan rivers) are located in northeastern Yunnan Province and western Guizhou Province, rise in the Maxiong Mountains, and drain the Yunnan–Guizhou Plateau. The Xi River basin as a whole drains the largest area of severely eroded karstic landforms in the world, and both upstream tributary basins are characterized by areas of strongly developed karst topography.

The Nanpan River exhibits a total length of 914 km, and possesses a drainage area of 56,880 km²; annual water discharge at its mouth is 242×10^8 m³/yr (table 1). The main first order tributaries (drainage area >1000 km²) are the Huangni, Mabie, Qingshui, Huaxi, and Dianxi rivers (Wei *et al.* 2013). Many hydropower stations have been constructed along the mainstream and its tributaries. These stations include the Xiqiao, Jiangbianjie, Tianshengqian, Lubuge, and Youjiazhai. In addition, the Huaxi River accepts water from Qilu Lake. Wanfeng Lake is also located along the lower reaches of the Nanpan River.

Table 1. Characteristics of the Nanpan and Beipan rivers (compiled from Lin *et al.* 2004; Tang and Mao 2004; Wang and Chen 2007; Xu and Liu 2007; Wang 2013; Wei *et al.* 2013; Wu *et al.* 2015).

Index	Nanpan River	Beipan River
Drainage area (km ²)	56,880	26,590
Discharge (m ³ /yr)	242×10^8	143×10^8
Total length (km)	914	444
Net primary productivity (g/m ² /yr)	1213.34	1079.18
Mean precipitation	1059	1255
Total fall (mm)	1854	1932
Carbonate proportion (%)	55.5	74.1
Slope > 25°	9486 (in Guizhou province)	
25° > slope > 6° (km ²)	29,104 (in Guizhou province)	
Slope ≤ 6°	9114 (in Guizhou province)	
Erosion areas (km ²)	14,715 (in Guizhou province)	
Agricultural areas (km ²)	38,100 (in Guizhou province)	
Industrial activities	Chemical fertilizer plant; paper industry; light industry	Coal-operated industries; electric power enterprises
Area of urban development (%)*	0.49	0.19
Cropland (%)*	63	44
Rock weathering rates (t/km ² /a)	77.4	103.3

*The data were obtained by GIS from ESA Globcover2009.V2.3.Global within the basin areas shown in figure 1(b).

The Beipan River is the largest tributary of the Nanpan River, and crosses the Yunnan, Guangxi and Guizhou provinces. The Beipan River possesses a total length of 444 km, and exhibits a drainage area of 26,590 km². Maximum altitude in the basin is 1932 m. Its annual water discharge is 143×10^8 m³/yr. The ecology and environment of the Beipan River basin is characterized by low vegetation-cover, wide valleys and high elevation karstic landforms. In comparison to the Nanpan River basin, these characteristics result in higher chemical weathering rates, more soil erosion and lower net primary productivity (NNP) (NPP is equal to 1079 g/m²/yr in the Nanpan River compared to 1213 g/m²/yr within the Beipan River) (Wang and Chen 2007; Xu and Liu 2007).

Geologically, the upper reaches of the Nanpan and Beipan rivers are underlain by detrital sedimentary rocks (shales, sandstones and siltstones) and igneous rocks (basic and ultrabasic rocks). In contrast, the middle and lower reaches of the catchments are dominated by Permian and Triassic carbonate rocks. Coal-bearing stratum is widely

distributed within the Beipan River Basin (Xu and Liu 2007).

Previous investigations have used major element and strontium (Sr) isotope geochemical data to assess the hydrogeochemistry, chemical weathering rates, and lithologic distributions within both the Nanpan and Beipan rivers and their tributaries (Xu and Liu 2007). However, the geochemistry and spatial variation of organic C within the upper reaches of the Xi River are not well known (Li *et al.* 2008). These data are especially lacking for the Nanpan River where single-event (snapshot) data are not even available. In contrast to the Beipan River, the Nanpan River flows through densely populated and industrialized cities, especially along its upper reaches (figure 1b) (Tao *et al.* 1997). Large quantities of industrial effluents are discharged into the river from these cities. Jing and Xu (2002) estimated that 50% of the effluent was derived from chemical engineering activities, while 37% was from light industry (mainly, tobacco, textile and paper mills). Approximately 2% was derived from coal effluents (Jing and Xu 2002).

Figure 1. (a) Map showing the location of the study area in southwest China; (b) map showing the sampling locations, sample numbers and distribution of soil types (Yao 2007) within the Nanpan and Beipan drainage basins. Guiyang: N: 26.35°, E: 106.42°. R: River.

The Nanpan River basin exhibits a total population of approximately 9.45 million. As a result, the amount of urban wastewater entering the river increases downstream within the Nanpan River (Wei *et al.* 2013). A large portion (80%) of the discharged urban effluent exceeded the discharge standard for organic compounds and toxic substances (Jing and Xu 2002). Arable terrains occupy 63% and 44% of the drainage areas of the Nanpan and Beipan rivers, respectively (table 1). Thus, in addition to urban inputs, agricultural non-point source pollution is a serious problem in both river basins.

3. Sample collection and laboratory analysis

3.1 Sample collection

Fourteen water samples were collected from the Nanpan River and 20 from Beipan River in July 2014 during the high-flow season (figure 1b). The water samples were collected from the surface to a depth of 0.5 m. Given the fine-grained nature of the particulate matter, it was assumed that both DOC and POC were homogeneously distributed within the water column (Horowitz *et al.* 1990), and that the samples are representative of the entire flow depth (which ranged between ~3 and 5 m). After collection, the samples were filtered through 0.7 μm pore size Whatman glass fiber filter papers (GF/F) that had been pre-weighed and combusted at 550°C for 6 hr. The particulate samples were collected from 0.45 μm pore size cellulose acetate filter membranes following the filtration of 5 l of river water; the filter paper was dried at 50°C and weighed to calculate suspended particulate matter (SPM). Filtrate, passed through GF/F filter papers, were acidified to a pH of <2 with 1–2 ml of 85% analytical phosphoric acid and kept in two 125 ml brown glass bottles in a refrigerator at 4°C for DOC analysis. Prior to use, the glass bottles were soaked in an acid solution for 24 hr and rinsed with ultrapure water after which they were rinsed 2 or 3 times with filtered river water.

3.2 Sample analysis

DOC concentrations were determined on an Aurora 1030W TOC Analyzer (IO). The method exhibited a precision of 0.01 mg/l. The SPM collected on the cellulose acetate filter was freeze-dried, scraped off and weighed to determine SPM concentrations. Then the SPM was decarbonated by HCl prior to the analysis of POC concentrations and $\delta^{13}\text{C}_{\text{POC}}$ values and C/N mass ratios. Both of the latter parameters (C, N) were determined by reference to a sulfanilamide standard consisting of 16.25% N and 41.81% C using an Elementar Vario MICRO cube. Replicate analysis indicated

a precision of $\leq \pm 0.5\%$. The C isotopic analysis (reported as $\delta^{13}\text{C}$) of the POC was determined by means of a iTOC-CRDS (Picarro, USA) coupled with Picarro ^{13}C Combustion Module. The analysis was calibrated against Urea1 (-34.22‰) and Urea2 (-8.02‰), and resulted in an analytical error of $\leq \pm 0.3\%$. The C isotopic ratios of the DOC were determined on a GasBench coupled with a MAT 253 mass spectrometer (with an error of 0.2‰; Zhou *et al.* 2015).

4. Results

4.1 DOC and POC contents

DOC concentrations ranged from 1.87 to 14.69 mg/l and 1.03 to 6.50 mg/l for the Nanpan and Beipan rivers, respectively (table 2). DOC concentrations for the Nanpan River were generally higher than for the Beipan River (figure 2a). POC concentrations varied between 1.00 and 8.42 mg/L for the Nanpan River. All but two samples from the mainstream of Beipan River exhibited undetectable POC concentrations due to limited SPM (concentrations of 0.2 to 2 mg/l in comparison to the tributaries which possessed concentrations of 2.8 to 947 mg/l). The POC values of the tributaries varied significantly, ranging from 0.09 to 19.82 mg/l. POC concentrations measured within tributaries to the Beipan River varied over a larger range than concentrations from tributaries within the Nanpan River Basin (table 2). The percent of POC contained within the SPM (POC%) varied from 0.59% to 3.25% and 0.21% to 3.61% for the Nanpan and Beipan rivers, respectively. These values are within the range observed for the Wu River where POC was thought to be derived from catchment soils (Tao *et al.* 2009).

DOC negatively correlated with POC within the Nanpan River Basin. This negative relationship implies that they are linked by means of a transformational relationship in which the degradation of POC produces DOC. A similar relationship between DOC and POC did not exist for the Beipan River; rather the plot between DOC and POC was characterized by significant scatter (figure 2a). In addition, along both the Nanpan and Beipan rivers, POC was positively correlated with SPM (figure 3), suggesting that POC was initially derived from SPM (Gao *et al.* 2002). The weight ratios of C/N ranged from 6.5 to 15.3 for the Nanpan River, while those for the Beipan River varied from 7.0 to 21.1.

4.2 C isotope composition of DOC and POC

The range of $\delta^{13}\text{C}$ values measured in DOC ($\delta^{13}\text{C}_{\text{DOC}}$) from the Nanpan River (-25.2 to

Table 2. Summary of geochemical data collected along the drainage system, including isotopic ($\delta^{13}\text{C}_{\text{POC}}$) and particulate organic carbon content (POC), organic carbon content (POC%), suspended particulate matters (SPM), and elemental (C/N mass ratio) composition of POC. Also included are dissolved organic carbon content (DOC), and the isotope composition of DOC of the Nanpan and Beipan rivers.

No.	River	Latitude	Longitude	SPM (mg/l)	DOC (mg/l)	POC (mg/l)	DOC/POC	POC (%)	C/N	$\delta^{13}\text{C}_{\text{DOC}}$ (‰)	$\delta^{13}\text{C}_{\text{POC}}$ (‰)
1	Nanpan River	N: 25°54.376'	E: 103°57.101'	1255.9	8.34	7.14	1.17	0.59	6.7	-24.9	-23.5
2	Nanpan River	N: 25°36.971'	E: 103°49.532'	74.9	11.25	2.44	4.61	3.25	10.4	-24.4	-21.9
3	Nanpan River	N: 25°17.512'	E: 103°51.405'	237.3	8.24	2.92	2.82	1.23	7.8	-24.4	-24.9
4	Nanpan River	N: 25°00.589'	E: 103°38.313'	159.5	14.69	4.11	3.57	2.58	10.8	-24.5	-25.7
5	Nanpan River	N: 24°56.169'	E: 103°10.674'	57.3	12.4	1	12.40	1.75	6.5	-24.2	-25.5
6	Nanpan River	N: 24°13.314'	E: 103°06.415'	539.2	10.41	5.78	1.80	1.07	7.7	-22.4	-22.7
7	Huaxi River	N: 24°12.664'	E: 103°06.806'	221.3	11.04	2.81	3.93	1.27	8.6	-24.1	-23.7
8	Dianxi River	N: 24°13.778'	E: 103°23.804'	254	8.13	4.41	1.84	1.74	12.1	-24.2	-24
9	Nanpan River	N: 24°39.293'	E: 104°28.732'	2.4	7.28	—	—	—	—	-25.2	—
10	Qingshui River	N: 24°39.257'	E: 104°28.790'	5.8	5.42	—	—	—	—	-24.3	-24.8
11	Huangni River	N: 24°46.524'	E: 104°32.253'	3.4	3.83	—	—	—	—	-24.9	-23.9
12	Wanfeng Lake	N: 24°52.129'	E: 105°01.755'	2.4	7.35	—	—	—	—	-25	-29.8
13	Mabie River	N: 25°11.607'	E: 104°54.663'	477.1	3.16	8.42	0.38	1.77	15.3	-24.2	-26.1
14	Nanpan River	N: 24°56.894'	E: 106°08.749'	2.5	1.87	—	—	—	—	-24.7	-24.8
15	Beipan River	N: 24°56.984'	E: 106°08.133'	2	1.84	—	—	—	—	-24.2	-25
16	Wangmo River	N: 25°09.598'	E: 106°05.519'	4.8	1.39	—	—	—	—	-24.6	-20.4
17	Zhelou River	N: 25°02.840'	E: 105°55.993'	3.6	1.25	—	—	—	—	-24.2	-25.4
18	Beipan River	N: 25°04.399'	E: 105°57.121'	14.6	1.06	0.03	35.33	0.21	7	-23.8	-25.6
19	Luofan River	N: 25°07.095'	E: 105°51.757'	*	1.05	*	*	*	*	-24.2	*
20	Groundwater	N: 25°06.965'	E: 105°51.617'	*	0.8	*	*	*	*	-23.8	*
21	Luofan River	N: 25°06.965'	E: 105°51.618'	51	1.03	0.74	1.39	1.44	7.2	-24.3	-22.2
22	Baiceng River	N: 25°22.678'	E: 105°47.127'	2.8	3.68	—	—	—	—	-22.3	-19.5
23	Baiceng River	N: 25°23.054'	E: 105°45.477'	9.7	3.72	0.15	24.80	1.55	8.5	-23.8	-24.6
24	Beipan River	N: 25°28.012'	E: 105°46.908'	0.4	3.83	—	—	—	—	-22.5	-9.6
25	Beipan River	N: 25°31.932'	E: 105°45.989'	0.2	4.43	—	—	—	—	-22.4	—
26	Dabang River	N: 25°52.383'	E: 105°40.367'	12.8	4.95	0.09	55.00	0.7	9.7	-24.6	-24.8
27	Dabang River	N: 25°53.339'	E: 105°38.595'	598.8	4.12	16.07	0.26	2.68	10.5	-21.6	-24.4
28	Baishui River	N: 26°00.774'	E: 105°40.083'	81	5.24	2.47	2.12	3.05	13.1	-21.8	-24.1
29	Beipan River	N: 25°40.338'	E: 105°39.591'	115.1	3.84	1.78	2.16	1.55	11.2	-24.1	-31.5
30	Zangke River	N: 26°10.138'	E: 105°11.266'	14.8	6.5	0.34	19.12	2.31	15.8	-24.9	-19.9
31	Baiche River	N: 26°26.503'	E: 105°04.567'	158.4	3.79	3.8	1.00	2.4	14.3	-25.2	-24.4
32	Balang River	N: 26°22.931'	E: 105°00.733'	13.8	2.71	0.5	5.42	3.61	19.2	-24.4	-24.5
33	Dadu River	N: 26°17.388'	E: 104°42.789'	946.7	3.64	19.82	0.18	2.09	21.1	-20	-25
34	Qingshui River	N: 26°00.141'	E: 104°30.067'	403.7	3.64	11.64	0.31	2.88	19.1	-23.4	-24.5

The “No.” is the sampling site shown in figure 1(b). The numbers from 1–14 are for the Nanpan River; the remaining are for the Beipan River. The Nanpan River waters are equally divided into two parts: upper (1–7) and lower (8–14) reaches. The 29 and its lower reach waters are regarded as lower Beipan River. —: undetected, *: no data, POC% = POC/SPM×100%.

Figure 2. Correlations between (a) POC and DOC concentrations and (b) POC and DOC $\delta^{13}C$ values.

Figure 3. Correlation diagrams of SPM and POC.

-22.4‰) was smaller than those observed for the Beipan River (-25.2 to -20‰). Values of $\delta^{13}C_{POC}$ also differed between the two rivers, ranging from -29.8 to -21.9‰ for the Nanpan River and -31.5 to -9.6‰ for the Beipan River. A portion of the $\delta^{13}C_{POC}$ values measured in samples from both rivers were similar to the $\delta^{13}C$ values associated with C_3 plants, the latter ranging from -24 to -30‰ (figure 2b). Other samples exhibited values that were between those of C_3 and C_4 plants. Sample 24 from the Beipan River exhibited a $\delta^{13}C_{POC}$ value of -9.6‰ , a value consistent to those of C_4 plants (-10 to -16‰) (Vogel 1993). These isotopic values indicate that C_4 plants (e.g., corn which is intensively grown in the region) are likely to a source of POC within the upper reaches of the Xi River (table 1). No significant correlations

existed between the isotopic values of DOC and POC for either the Nanpan or Beipan River (figure 2b).

5. Discussion

5.1 Spatial DOC and POC distribution

DOC concentrations decreased downstream within both the Nanpan and Beipan rivers (table 2; figure 1b). Within the Beipan River, DOC varied within the narrow range of 2.71 – 5.24 mg/l upstream of its confluence with the Baiceng River – a tributary (figure 1). An exception was water from the Zangke River scenic spot. Water at this site was characterized by a relatively high DOC content (6.5 mg/l), potentially reflecting higher anthropogenic inputs of DOC than along other reaches characterized by lower values. DOC concentrations measured along reaches below the Beipan–Luofan River confluence (figure 1) were relatively low. These values are similar to the DOC concentrations found in groundwater (sample 20; around 0.8 mg/l), suggesting that the influx of DOC was limited to base flow. Within the Nanpan River basin, highly urbanized reaches upstream of the Huaxi River (figure 1) possessed higher DOC contents than in other carbonate-dominated areas of the upper Xi River basin.

DOC/POC ratios often reflect the current state of soil erosion, vegetation and degree of pollution within a drainage basin (Gao *et al.* 2002). In regions characterized by monsoonal climates the DOC/POC ratios should be <1 (Kao and Liu 1996; Ludwig *et al.* 1996). However, this is not the case for either the Nanpan or Beipan rivers. The DOC/POC ratios for the Nanpan River were typically higher than 1.18 (the world's average value) (Ludwig *et al.* 1996); the maximum DOC/POC ratio was 12.34 . This maximum value is close to the ratio generally observed in lakes (DOC/POC = 10) (Schlesinger and Melack 1981; Westerhoff and Anning 2000), such as Qinghai Lake located in the northeastern section of the Qinghai–Tibet plateau (Xu *et al.* 2013). The observed DOC/POC values imply that lakes, dams, and other types of surface water impoundments decrease water velocity, increase C residence time, and slow down the decomposition rates of organic matter (Zhang *et al.* 2009). The organic matter detained within the lakes release dissolved C (Ittekkot and Arain 1986) thereby elevating DOC/POC ratios. If it were not for the input of DOC from the lakes, DOC/POC ratios would quickly be reduced to the average of the world's rivers (1.18).

With regard to the Beipan River, characteristics of the organic C within the water column differed between the mainstream and its tributaries.

POC values along the mainstream of the river were generally below detection, presumably because of low SPM concentrations. However, the tributaries draining upland areas differed between the two rivers. In contrast to the Nanpan River, DOC/POC ratios within tributaries of the Beipan River varied over a broad range (0.18–55), and were relatively low. The lower DOC/POC ratios observed along the tributaries of the Beipan River suggest that the primary source of organic C was the severe erosion of catchment soils during intense monsoonal runoff events. This hypothesis is supported by data collected in other heavily eroded catchments in China. For example, water within the highly eroded Yellow River Basin exhibited DOC/POC ratios as low as 0.03 (Zhang *et al.* 2013). The higher ratios observed for the Beipan River may be attributed to the leaching of DOC from soils during less intense events that were incapable of generating significant soil erosion (and POC). Thus, the large variations in DOC/POC ratios within tributaries of the Beipan River appear to be strongly controlled by temporal variations in runoff and soil erosion associated with the region's monsoonal climate.

5.2 Isotopic characteristics of DOC and POC

The $\delta^{13}\text{C}$ values of DOC were less negative than for POC within both the Nanpan and Beipan rivers, and more positive than the $\delta^{13}\text{C}$ values of phytoplankton (-29.7‰ ; Li 2009). These trends suggest terrestrial C inputs were mostly derived from C_3 vegetation during the wet season (figure 2b). A similar conclusion was reached for the Wu and Yuan rivers by Liu (2007). Similarly, Palmer *et al.* (2001) found that the $\delta^{13}\text{C}_{\text{POC}}$ for terrestrial plants exceeded -30‰ , whereas $\delta^{13}\text{C}_{\text{POC}}$ was less than -30‰ for aquatic plants within the Brocky Burn watershed of northeast Scotland.

A negative relation ($R=0.68$) was observed between POC and DOC in the Nanpan River (figure 2a). This indirect relationship may indicate that POC was transformed into DOC through degradation. Moreover, a weak correlation exists between $\delta^{13}\text{C}$ values of DOC and POC ($R=0.41$; figure 2b), implying $\delta^{13}\text{C}$ values are inherited from the POC. This follows because there is typically a much lower degree of fractionation associated with degradation than photosynthesis. In addition, while values of $\delta^{13}\text{C}_{\text{POC}}$ varied, they overlapped with the typical $\delta^{13}\text{C}$ values associated with catchment soil in southwest China, such as those studied in Guiyang (-24.8 to -21.1‰ ; Zhu and Liu 2006) and Maolan (-23.3 to -29.1‰ ; Han *et al.* 2015). These data, then, indicate that soil C degraded to DOC within the water column, and that this process is an important means through which POC is consumed and DOC produced in the Nanpan

River. Moreover, the degradation of soil C in river waters, and the production of DOC results in much higher DOC than POC, concentrations, and higher DOC/POC ratios.

The pattern of isotopic values observed for the Nanpan River was not present along the Beipan River. The narrow range of $\delta^{13}\text{C}_{\text{DOC}}$ values observed for the Nanpan River is probably related to the input of DOC from a single agrottype within the basin (figure 1b; Yao 2007). The wider range of $\delta^{13}\text{C}_{\text{DOC}}$ values measured within the Beipan River may have been caused by the leaching of DOC from multiple catchment soil types during severe soil erosion events.

The combined examination of $\delta^{13}\text{C}$ and C/N ratios has been used as a powerful tool to interpret potential sources of POC in rivers (Andrews *et al.* 1998; Wang *et al.* 2004; Xiao and Liu 2010; figure 4). The C/N ratios of C_3 and C_4 plants are generally higher than 15 (Kendall *et al.* 2001). Bacteria have C/N ratios varying from 2.6 to 4.3. Soil organic matter and phytoplankton in karstic areas are characterized by a unique range of $\delta^{13}\text{C}$ and C/N values. For soil organic matter, $\delta^{13}\text{C}$ and C/N values range between -27.1 and -21.1‰ and 8 to 14, respectively. In contrast, $\delta^{13}\text{C}$ values range between -22.97 and -35.03‰ for phytoplankton, while C/N values vary from 1 to 8 (Balakrishna and Probst 2005; Zhu and Liu 2006; Li 2009). Due to the relatively constant release of organic C from channel-bed sediments (Tao 1998), the allochthonous input of organic C by surface runoff is usually the dominant source of POC during the wet summer months (Tao *et al.* 2009). As shown in figure 4, allochthonous C (SOC and terrestrial plants) was the primary source of POC to the Beipan River. Most of the POC in the Nanpan River was derived from SOC and autochthonous C (phytoplankton). The $\delta^{13}\text{C}$ and C/N ratios of sampling point 29 (figure 4) probably resulted from the mixing of phytoplankton and other sources because the $\delta^{13}\text{C}_{\text{POC}}$ value was lower than -30‰ . The downstream reaches of the Beipan River are characterized by relatively low concentrations of

Figure 4. Correlation diagram of $\delta^{13}\text{C}_{\text{POC}}$ and C/N.

SPM. These particulates were characterized by C/N ratios that were less than 8, indicating increased contributions of C from *in situ* phytoplankton (figure 5). The C/N ratios along the upper reaches of the Beipan River were higher than 10. Previous studies showed that ploughed slopes within the Guizhou Mountains exhibit gradients between 6° and 25°, and covered an area of 29,104 km² (table 1). Large quantities of undegraded plant detritus mixed with slope-derived farmland soil are therefore likely to be major sources of POC to the river during runoff events (table 1; Lin *et al.* 2004; Tao *et al.* 2009). The POC from terrestrial C is characterized by an average $\delta^{13}\text{C}_{\text{POC}}$ value of −23‰ during extreme flood events where

Figure 5. Spatial variations of C/N along the Nanpan and Beipan rivers.

there is little primary production (in-river photosynthesis). The $\delta^{13}\text{C}$ value of primary production in the Xi River can be as low as −32‰ (Sun *et al.* 2011). The average $\delta^{13}\text{C}_{\text{POC}}$ value of the Nanpan and Beipan rivers were −24.7 and −23.3‰, respectively (calculated from table 2).

The $\delta^{13}\text{C}$ value of riverine POC derived from terrestrial C can be estimated by the following isotopic mass balance:

$$\delta^{13}\text{C}_{\text{POC}} = f_{\text{au}} \cdot \delta^{13}\text{C}_{\text{au}} + f_{\text{al}} \cdot \delta^{13}\text{C}_{\text{al}}$$

and

$$f_{\text{au}} + f_{\text{al}} = 1,$$

where *f* is the proportion of autochthonous (au) and allochthonous (al) C. Accordingly, the results show that 81% and 97% of the POC was derived from terrestrial sources for the Nanpan and Beipan rivers, respectively. This is consistent with the occurrence of severe soil erosion in the upper reaches of the Xi River. The $\delta^{13}\text{C}_{\text{POC}}$ values were higher within our study areas than within the Wu and Yuan river basins. The latter two rivers typical exhibited $\delta^{13}\text{C}_{\text{POC}}$ values indicative of terrestrial C sources (soil, higher plants) and phytoplankton (figure 4; Tao *et al.* 2009). The results indicate that land-use changes that promote C4 plants (e.g., corn and grasses) deliver more POC characterized by heavier $\delta^{13}\text{C}_{\text{POC}}$ values to the rivers (figure 6).

Figure 6. Schematic diagram summarizing sources of organic carbon to the Nanpan and Beipan rivers.

6. Conclusions

Spatial variations in POC and DOC content, C/N ratios, and DOC/POC ratios as well as the C isotopic signatures of POC and DOC within two headwater tributaries to the Xi River basin were used to assess the primary sources of organic C within basins of southwest China characterized by a monsoon climate. The highly urbanized Nanpan River possessed higher DOC contents than the Beipan River. Both rivers show similar downstream decreasing trends in DOC concentration. DOC/POC ratios for the Nanpan River were generally higher than the world average for rivers, presumably due to the interception of water and C by dams and other hydrological structures. These structures increased the residence time of C within the river system and promoted the degradation of POC (and the formation of DOC) within Nanpan River waters. DOC/POC ratios for the mainstream of the Beipan River could not be calculated, presumably because of low SPM concentrations. However, tributaries to the Beipan River were highly variable and exhibited the lowest DOC/POC ratio (0.18). The observed values can be attributed to the highly variable input of allochthonous upland C, primarily POC from eroded soil, during intense runoff events associated with the region's monsoonal climate. DOC in the Beipan River also appears to have been associated with runoff events, in this case the leaching of C from catchment soils. Allochthonous inputs were also the dominant source of organic C within to the Nanpan River. Among them, soil C that degraded to DOC within the water column was an important source. The degradation process consumed POC and produced DOC. In contrast to the Beipan River, aquatic C appears on the basis of C isotopic and C/N data to have been another source of POC in the Nanpan River.

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