ISSN 0016-7029, Geochemistry International, 2018, Vol. 56, No. 5, pp. 462–473. © Pleiades Publishing, Ltd., 2018.

The Response of Carbon Geochemistry to Hydrological Events within an Urban River, Southwestern China[1]

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Received February 17, 2017; in final form, March 14, 2017

Abstract—Natural and anthropogenic impacts on dissolved inorganic carbon (DIC) within an urban river, Nanming River in southwestern China, were investigated using hydrochemistry and carbon isotopic compositions of dissolved inorganic carbon ($\delta^{13}C_{DIC}$). Because of the anthropogenic inputs, generally, the TDS values and major ionic compositions showed an increasing trend along the mainstream. The TDS values and most of the dissolved solutes compositions showed a dilution effect during storms, but the dilution effect did not strictly follow the theoretical dilution curve. Lighter $\delta^{13}C_{DIC}$ values in the river after a rainstorm reflected the influx of rain water with biological CO_2 during the rain event. Meanwhile, the negative relationship between $\delta^{13}C_{DIC}$ values and dissolved inorganic carbon concentrations in the mainstream at different sampling campaigns suggested significant degradation of organic matter in the riverine channels. The variabilities of DIC in an urban river were mainly impacted by biological activities and infiltration of soil carbon dioxide. This study demonstrated that hydrological events and anthropogenic inputs are the main controls on the variations of dissolved solutes compositions and the DIC dynamics for an urban river.

Keywords: anthropogenic impacts, $\delta^{13}C_{DIC}$, DIC dynamics, hydrochemistry, rainstorm, urban river

DOI: 10.1134/S0016702918050099

1. INTRODUCTION

Riverine loads reflect biogeochemical processes in catchment areas and help quantify material transport from the land to the ocean (Barth et al., 2003). The riverine transport of dissolved and particulate materials is generally related to a large number of interactions involving climate, hydrological, physico-chemical, and biological aspects (Buccianti et al., 2008). However, these processes are fragile and easily disturbed by urban activities and climatic events. Urban inputs and rainstorms play an important role in the chemical compositions and affect the carbon biogeochemical cycle (Dong et al., 2015). Meanwhile, the urban river is closely related with the social and ecological functions of the development of a city, as well as the health and living of its inhabitants. Therefore, investigating the biogeochemical processes of urban rivers is significant for understanding the status of the ecosystem. Though several studies have focused on the hydrochemistry and biogeochemical cycle of the river (Gaillardet et al., 1999; Han and Liu, 2004; Li et al., 2010; Pipko et al., 2010), few studies have focused on the effects on the hydrochemistry and carbon biogeochemical processes in the urban river (Barnes and Raymond, 2009). Solute concentrations in surface waters are temporally dynamic during hydrological events, particularly during storm periods when soil water conditions vary along the primary flow path (Dinsmore et al., 2011). Nevertheless, as several researchers have noted, it is often difficult to separate the human impact on the riverine constituents and ecology due to the highly correlated nature of land use, geology, soils, and climate (Barnes and Raymond, 2009). Hence, great attention should be paid to the hydrochemistry and biogeochemistry cycles of urban rivers during rainstorm events. It is vital to study the geochemical response for the hydrological events of an urban river, especially in southwestern China, an area where some of the fastest urbanization is occurring. Nanming River is affected by both natural monsoons and long-term man-made changes, both of which are likely to affect the dissolved solutes and the variabilities of carbon dynamics.

Hydrochemistry and isotopic compositions of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) in water samples are useful for understanding riverine hydro-geochemistry and biogeochemical processes (Hélie et al., 2002; Li

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et al., 2005). Chemical weathering of carbonates and silicates, carbon dioxide (CO_2) exchange with the atmosphere, bacterial oxidation of organic matter in rivers, photosynthesis, precipitation, or dissolution of carbonates are factors affecting riverine dissolved inorganic carbon (DIC) dynamics. Chemical weathering is a key part of the global carbon biogeochemical cycle, which links rocks and the atmosphere to the rivers. Chemical weathering of rocks by carbonic acid sequestrates atmospheric CO_2 and contributes major dissolved loads to rivers. However, water chemistry and riverine carbon (C) fluxes are very sensitive to regional and global change due to the fact that riverine fluxes reflect physical, biotic, and anthropogenic processes (Barnes and Raymond, 2009). Barnes and Raymond (2009) found that urban activities increase DIC influxes. Across system variation in the C flux from the watershed is strongly correlated with precipitation (Raymond and Oh, 2007). Dilution effects are common in response to high levels of precipitation during summer in the karst areas of southwest China (Li et al., 2010). Within a watershed, the annual variation in precipitation is also a driver of the annual C export (Raymond and Oh, 2007). Therefore, in order to relate water quality problems with their carbon sources, we need better understand the changes in carbon dynamics over sequences of hydrological events across urban catchment scales. The carbon dynamics of the Nanming River during rainstorm events represent a complex set of interactions between urban activities, event characteristics, and the lithology of the drainage catchments.

This study investigated the hydrochemistry and $\delta^{13}C_{DIC}$ values for the Nanming River, which is an urban river that flows through Guiyang city in southwestern China. The objectives of this study were to (1) analyze the temporal and spatial variations of major ions in the urban river during hydrological events; (2) assess the effects of urban activities and hydrological events on the hydrochemistry and biogeochemical processes; and (3) examine how urban activities and hydrological events affect inorganic carbon dynamics.

2. STUDY AREA

Guizhou Province, Southwestern China, is located in the center of the Southeastern Asian Karst region, which is the largest karst area in the world. Guiyang is the capital city of Guizhou province, located on the southwestern China plateau, covering an area from 26°11′00″ to 26°54′20″ N and 106°27′20″ to 107°03'00" E, and ranging from 875 to 1655 m above mean sea level (Lang et al., 2006). Guiyang is 8034 km^2 with a downtown area of 2403 km^2 (Mostofa et al., 2010), and the urban population is close to 3 million. The climate of Guiyang is a subtropical monsoon with an average temperature of 15.3°C, annual rainfall of 1174 mm, and a relative humidity of about 77% (Xiao et al., 2012). The seasonal monsoonal climate often results in more than 80% of the annual precipitation. As a subtropical-tropical urban river with high population, intense continental erosion, plentiful rainfall, and intense anthropogenic activities, the Nanming River flows through Guiyang city (Fig. 1a) with a drainage area of 1433 km^2 and two main tributaries (Xiaoche River and Shixi River). The Nanming River is a tributary of Qingshuijiang River, and is associated with the Wujiang River catchment. The Shixi River is heavily polluted by urban activities, and the Xiaoche River is derived from the Aha reservoir, providing drinking water for Guiyang inhabitants. The Nanming River originates from Huaxi town, and passes through Guiyang City from the southwest to the northeast. The carbonate rocks are widely exposed in the drainage area. The Guizhou province is mainly covered with C_3 plants (Liu, 2007, 2009; Li et al., 2010). The banks of Nanming River in the urban area were artificially built with concrete, so the sources of chemical weathering could be ignored. A large volume of untreated municipal and industrial effluents commonly discharged into the rivers and lakes in China (Mostofa et al., 2010). Municipal sewage discharged from enterprises, factories, and households on both sides of the Nanming River gives rise to complicated sources of pollutants in the surface/ground water (Lang et al., 2006). The rainwater flushes the surface of the ground when it rains, Meanwhile, a large volume of pollutants in the urban area was flushed out by the rainwater, and then discharged into the river during a rainstorm.

3. METHODOLOGY

3.1. Sampling Methods

A series of sampling campaigns were conducted in the Nanming River, and eight sampling sites in the mainstream and two sites in the tributaries (Xiaoche and Shixi River, respectively) were chosen (Fig. 1a). Riverine water samples were collected for hydrochemical and isotopic analysis during August to October in 2011, corresponding to hydrological variations. M1, located on the upstream of the Nanming River, reflects the effects of natural erosion and weathering. M2 to M5 are located in a densely populated area, and are affected by intense anthropogenic activities. Though M6, M7, and M8 are located in a sparsely populated area, they are affected by industrial impacts at the lower reaches of Nanming River, So M2–M8 are intensely affected by anthropogenic inputs. The sampling times are shown on the horizontal ordinate (Fig. 1b): N1 was sampled two days after a 528 mm/day rainstorm, but the discharge showed the lowest value. N4 and N6 were sampled after rainstorm of 171 and 618 mm/day, respectively, which triggered the high discharge of Nanming River during the sampling cam-

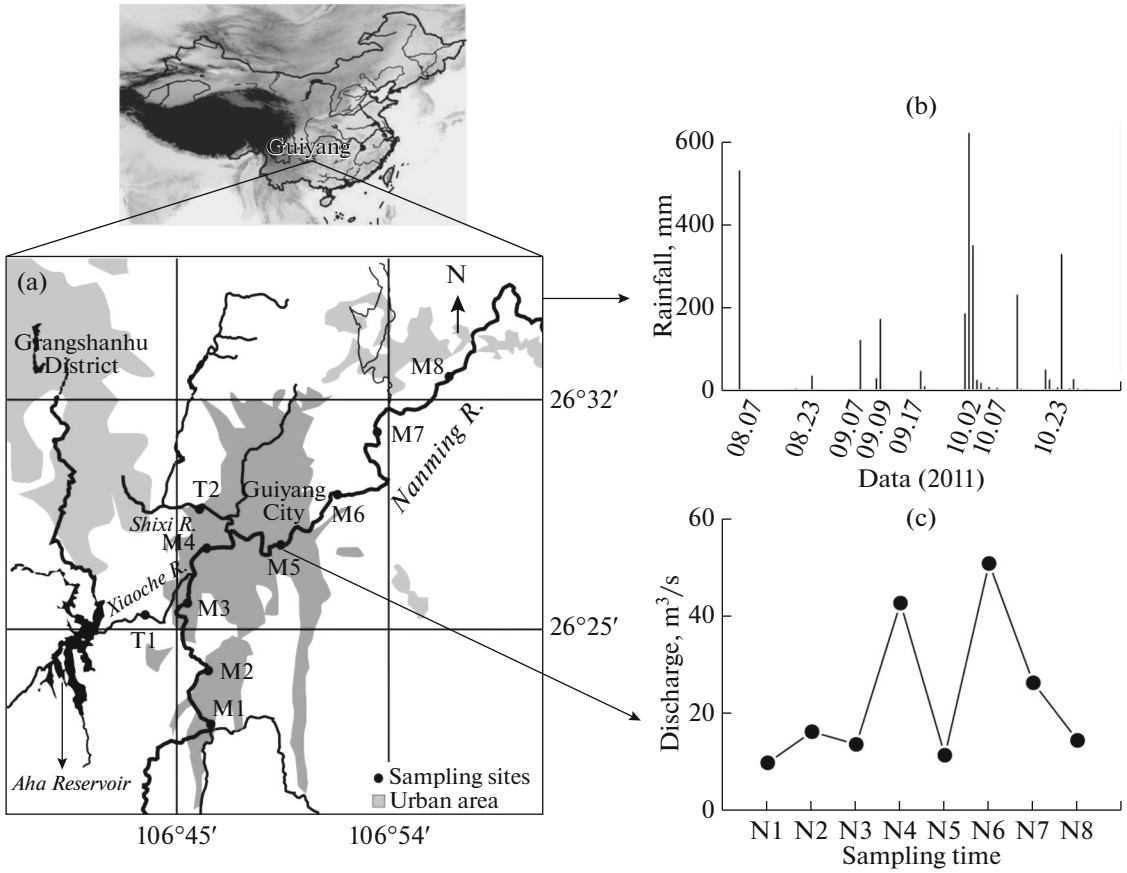

Fig. 1. (a) Location of sampling sites in the Nanming River catchment, Guiyang City, southwestern China. M1 to M8 represent the sampling sites in the mainstream from upper reach to lower reach. T1 and T2 represent the tributary sampling sites, located in the Xiaoche and Shixi River respectively. We collected riverine water samples 8 times, N1–N8 represent the sampling times. (b) Represents the precipitation during the sampling times. (c) shows the discharge of the M5, M6, M7, and M8.

paigns. Figure 1c shows the discharge of sampling time, which is measured at site M5. Because of the fast water velocity and shallow depth of the river, there is no lateral and vertical stratification of the river water. Water samples were taken Samples were collected in 1.5 L pre-cleaned high-density polyethylene (HDPE) bottle free of air. In addition, many samples of rainwater, sewage, and runoff water, running on the surface of road after rainstorm, were collected to assist the work. Temperature (T), pH, and electrical conductivity (Ec) were measured in the field. The discharge was determined using the buoy method of flow measurement at site M5. The flow velocity varied between 0.28 to 1.08 m/s within the sampling time. Because there are no large tributaries inflowing into the mainstream and a short distance between them, M6–M8 share the same discharge as M5.

3.2. Analysis Methods

The alkalinity was determined by Gran titration with 0.02 M HCl after sampling in 24 hours. Major ion concentrations of the samples were measured after being filtered through 0.45 um cellulose acetate filters. For the major cations (calcium, Ca^{2+}, sodium, Na^{+}, potassium, K^{+}, and magnesium, Mg^{2+}) analysis, samples were acidified using ultra-pure nitric acid to pH < 2 and determined by ICP-OES,and major anions (sulfate, SO_4^{2-}, chloride, Cl^{-}, fluoride, F^{-} and nitrate, NO_3^{-}) were analyzed using a Dionex ICS 90. Precision for all major ions was better than 5%. The CO_2 from DIC was extracted in the off-line vacuum system according to the method in a previous study (Li et al., 2005), and the carbon isotope ratios of CO_2 were determined by MAT 252 mass spectrometer with the δ notation relative to PDB in per mil (Li et al., 2010). Routine $\delta^{13}C_{DIC}$ measurements had an overall precision of 0.1%. We distinguished the DIC species with alkaline, pH, and temperature using mass action relationships and the relative equilibrium constants. All of these measurements were performed in the State Key Laboratory of Environmental Geochemistry, Guiyang, China.

Solute concentrations in riverine waters are temporally dynamic during hydrological events, particularly

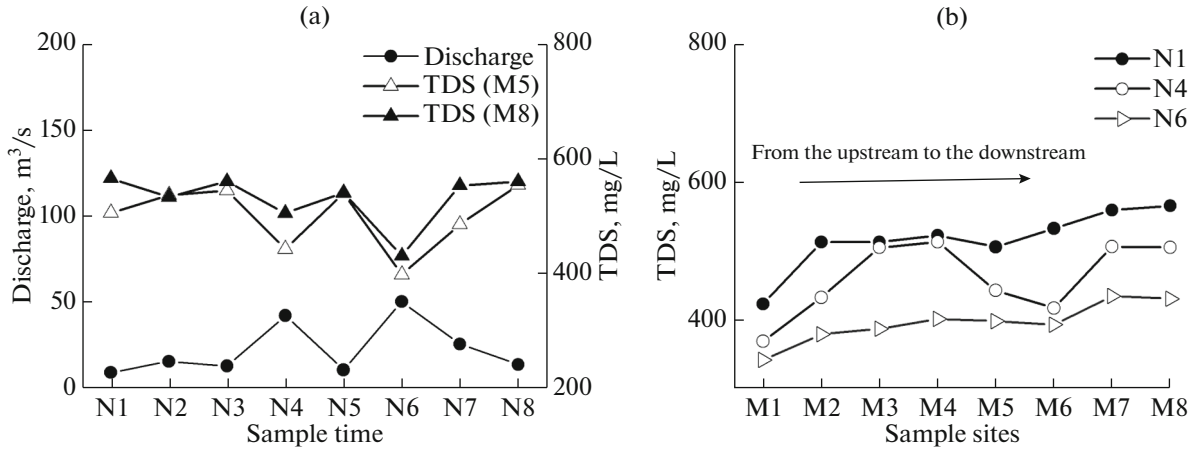

Fig. 2. (a) Temporal variations of TDS vs. discharge at site M5 and M8. (b) Variations of the TDS from upstream to downstream in the Nanming River for N1, N4, and N6, respectively.

during rainstorms. Assuming the solute is conservative and is not being actively removed from the river, decreasing concentrations are the result of dilution as the primary flow path moves away from the zone of solute production (Dinsmore et al., 2011). There is a power-law relationship between concentrations of dissolved solutes and discharge:

$$C_i = aQ_i^b. \quad (1)$$

Where C_i represents the concentrations of dissolved solutes, Q_i represents the water discharge, and a and b are the regression coefficients. When b is near -1, the fluxes of the solutes are constant, indicating that the sources of the dissolved solutes are independent from the hydrological processes and the hydrological regime, which suggests that fluxes of dissolved solutes are constant despite variations of precipitations and discharge. When b is near 0, the concentrations of the solutes are constant, indicating the flux of the solutes only depends on discharge, and there is no dilution effect during a rainstorm. In the case of the theoretical dilution curve, the b value is equal to -1.

4. RESULTS AND DISCUSSION

4.1. The Temporal and Spatial Variations of Major Ions

The riverine water samples of the Nanming River were mildly alkaline: The pH values in the mainstream ranged from 7.5 to 8.0, with an average value of 7.7, which was much lower than the Wujiang River (8.4) (Han and Liu, 2004); the pH ranged from 7.6 to 8.0 and from 7.1 to 7.8, respectively, for the Xiaoche and Shixi Rivers. The EC had a wide range, which varied from 439 to 832 μS/cm. Owing to the dilution effect, the relative lower values were witnessed after a rainstorm. Nevertheless, the largest value of EC was attained on N2–M8 due to the effects of drought and anthropogenic activities. The total cationic charge (TZ^+) ranged from 5.52 to 8.08 meq/L, with an average value of 6.84 meq/L, which was higher than the value of the average Changjiang River (2.80 meq/L (Chen et al., 2002) and Wujiang River (4.14 meq/L (Han and Liu, 2004)). The TZ^+ values increased from the upper reaches to the lower reaches of the Nanming River, the same as TZ^-, because of the increased anthropogenic inputs.

The values of the total dissolved solutes (TDS = $Na^+ + Ca^{2+} + K^+ + Mg^{2+} + Cl^- + SO_4^{2-} + HCO_3^- + NO_3^- + SiO_2$, in mg/L) not only reflect the different lithologies drained by the river, but also can be used as an index of land use and the effects of human activities on the water quality (Gaillardet et al., 1999; Chetelat et al., 2008). The TDS values of the riverine water samples varied between 346.59 and 627.66 mg/L, with an average of 508.21 mg/L. Compared to other rivers draining carbonate terrains (Karim and Veizer, 2000), the Nanming River had relative high TDS values, which also included Wujiang River (373 mg/L (Han et al., 2010)). The TDS of running water on the road surface during the rainstorm were lower values, ranging from 80.0 to 189.1 mg/L, with an average value of 134.3 mg/L. The TDS values of rain water ranged from 17.7 to 66.3 mg/L, with a median value of 34.9 mg/L. The relatively higher TDS values in the Nanming River were likely due to not only the carbonate lithology being drained but also the anthropogenic inputs.

The greatest temporal variations of TDS in riverine water occurred after rainstorm events, and the values measured at M5 were much lower than at site M8 (Fig. 2a). Site M5 is located at the center of Guiyang city, and urban runoff along the street flowed directly into rivers while the rainstorm occurred. Although site M8 is located in a sparsely populated area downstream, a large volume of untreated point pollution water from the industrial district flows into the river,

which can reduce the dilution effect of the rainstorm. Thus, site M5 was witnessed the effect of dilution more obviously, compared with site M8. Due to the dilution effect and little anthropogenic inputs, the lowest TDS value was observed on N6–M1 (Fig. 2b). In general, the TDS values of riverine water on the mainstream increased from the upstream to the downstream in the Nanming River, mainly, due to the increasing anthropogenic inputs along the mainstream. Due to the similar TDS values and the relatively smaller discharge from the tributaries, when the tributaries (with average TDS values of 542.94 and 473.94 mg/L, respectively) flowed into the mainstream, the TDS values in the mainstream had no significant variation.

The dissolved solute concentration of riverine water samples showed significant spatial variations along the mainstream. In general, the concentrations of the major ions increased gradually from the upper reach to the lower reach. The increasing concentrations of K^+, SO_4^{2-}, Na^+, Cl^-, Mg^{2+}, and Ca^{2+} from upstream to downstream should be ascribed to the anthropogenic inputs, and biological activity should respond to the increasing concentration of HCO_3^-. However, Mg^{2+}, Ca^{2+}, and HCO_3^- did not show an increasing trend on the mainstream as obviously as the other ions. Most of the water samples in Nanming River had calcite saturation indexes (SIc) and dolomite saturation indexes (DIc) above zero, indicating calcite and dolomite precipitation occurred in the river with increasing anthropogenic sources of Ca^{2+} and Mg^{2+}, as well as biological sources of HCO_3^- along the mainstream.

In general, the major ion concentrations of the Nanming River followed this pattern: $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ for the cations, $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > F^-$ for the anions, which was different from most of the natural large rivers in the world (Gaillardet et al., 1999). The studies revealed that HCO_3^- and SO_4^{2-} were the dominant anions for the riverine water samples, which varied from 72.0 to 92.5% (with a mean value of 85.4%) for the total anions. Ca was dominant of the cations, and accounted for 39.2 to 61.8% for all of the samples, with an average value of 53.1% on the mainstream. In the study area, Ca would mainly derive from carbonate weathering, silicate weathering, and anthropogenic inputs, since carbonate weathering occurs more easily than silicate weathering and limestone is widely distributed in this region, which corresponds to the typical characteristics of the major ion compositions of riverine water in the Guizhou karst area (Han et al., 2010). Carbonate weathering by carbonic acid and sulfuric acid may be responsible for the characteristics of the ions. The concentrations of Ca in the Xiaoche River were higher than in the Nanming River, and the concentrations of Na were lower, which was mainly ascribed to relevant procedures conducted to protect the water quality of the Aha reservoir and the function of self-purification in the reservoir. Therefore, relative low concentrations of the major ions were found in the Xiaoche River, as well as the little sources of anthropogenic inputs.

4.2. The Dilution Effect of the Dissolved Solutes

Climate and geology are the most important controlling factors in hydrochemistry in many rivers (Han and Liu, 2004; Skoulikidis, 2009; Li et al., 2010). Geochemical and hydrogeological variability, as well as precipitation patterns, affect water temperature and solute concentrations (Skoulikidis, 2009). During the monsoon season, the high discharge reflects the input of precipitation. It has been long noted that solute concentrations vary systematically with respect to rising and falling limb discharge on the storm hydrograph (Rose, 2003).

The rainstorm events can bring dilution effects, hydrodynamic effects, and pollution effects to the river. Dilution effects: the ion concentrations can be diluted by the rainwater, which has a relatively lower concentration. Hydrodynamic effects: the rate of chemical weathering and physical erosion become more intense due to the scouring action of the rain water. Pollution effects: the rainwater scours the surficial ground, and a large amount of pollutants are injected into the river with the surface runoff. TDS, Na^+, Ca^{2+}, Cl^-, and HCO_3^- demonstrated negative correlations with discharge (Fig. 3), indicating TDS, Na^+, Ca^{2+}, Cl^-, and HCO_3^- tended to follow a dilution effect. However, the dilution effect did not strictly follow the theoretical dilution curve. The power function provided a good negative relation between concentrations and discharge (Fig. 3), and the solutes presented a significant relation following Eq. (1). The values of b varied from –0.4 to 0, representing the common influence of both the dilution effect and the injected pollutants on the hydrochemistry of riverine water. The concentrations of dissolved solutes at M5 were much lower than those at M8, and showed a more obvious dilution effect.

4.3. The DIC Dynamics Responding to Hydrological Events for an Urban River

4.3.1. Characteristics of the DIC for the riverine water. The DIC is the sum of CO_2 (aq), carbonic acid (H_2CO_3), HCO_3^-, and carbonate (CO_3^{2-}) ions (Li et al., 2010). The DIC values of the Nanming River varied from 1.88 to 5.42 mmol/L, with an average value of 3.32 mmol/L. The riverine DIC contents showed a slight increased trend from the upper reach to the lower reach in the urban area, especially at the down-

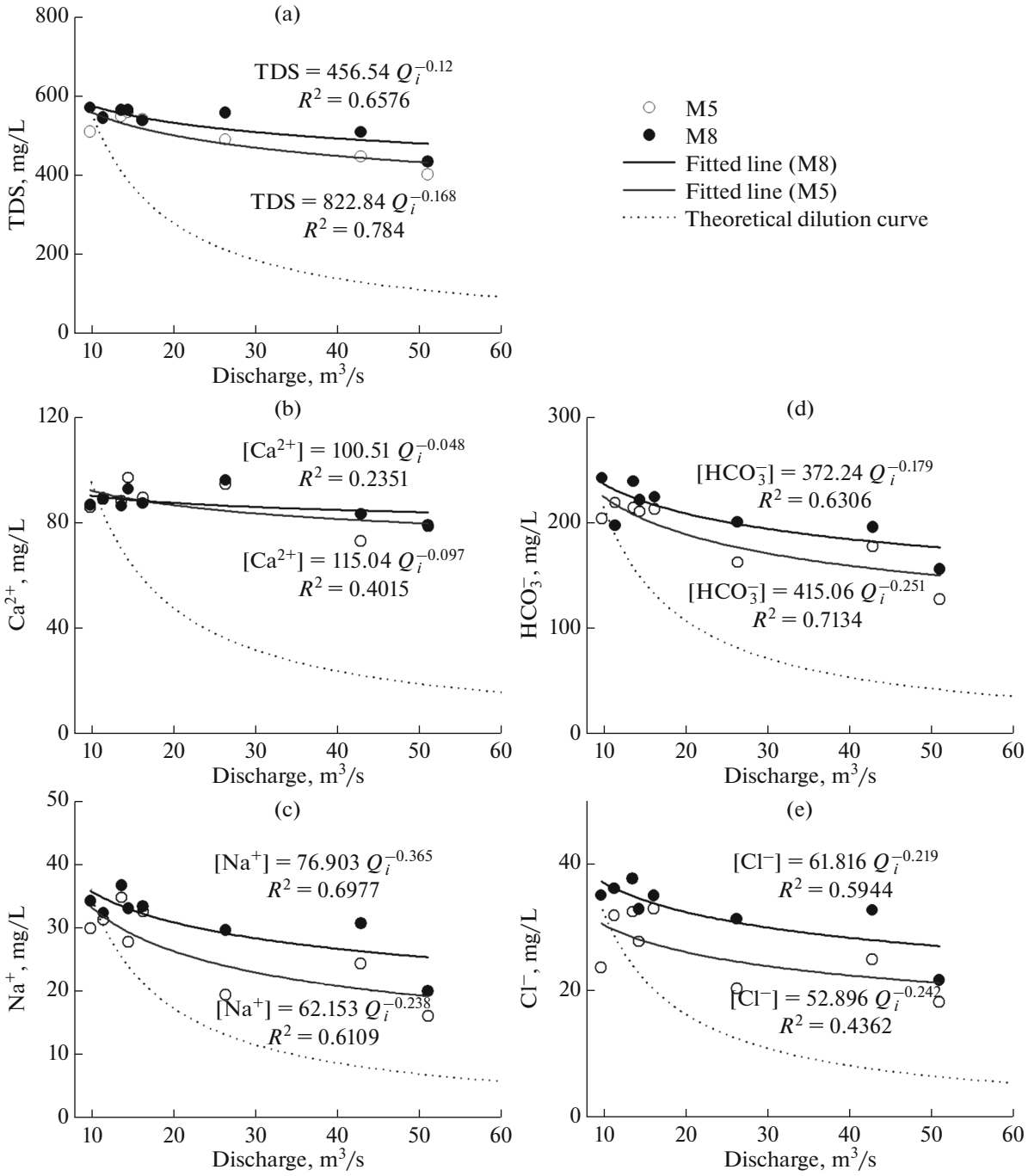

Fig. 3. Concentrations of TDS (a), Ca^{2+} (b), Na^+ (c), HCO_3^- (d), and Cl^- (e) vs daily discharges.

stream (after M5) (Fig. 4), indicating Eqs. (2), (3) occurred along the mainstream. From the upper reach to the lower reach, increasing urban organic matters were poured into the river, and increasing DIC contents from biological activities were produced. Figure 4b showed that the DIC values decreased after a rainstorm, which could be ascribed to the dilution effect. However, there were inconspicuous temporal variations of DIC content on T1 for the impoundment effect of the Aha reservoir. The highest and the lowest DIC values of the Nanming River were observed on N1–M8 and N6–M1, respectively, with the lowest and largest discharge. DIC species calculations suggested that HCO_3^- was the most abundant carbonate species. HCO_3^- accounted for up to 90% in all of the samples, and CO_3^{2-}, rarely, contributed to the DIC of

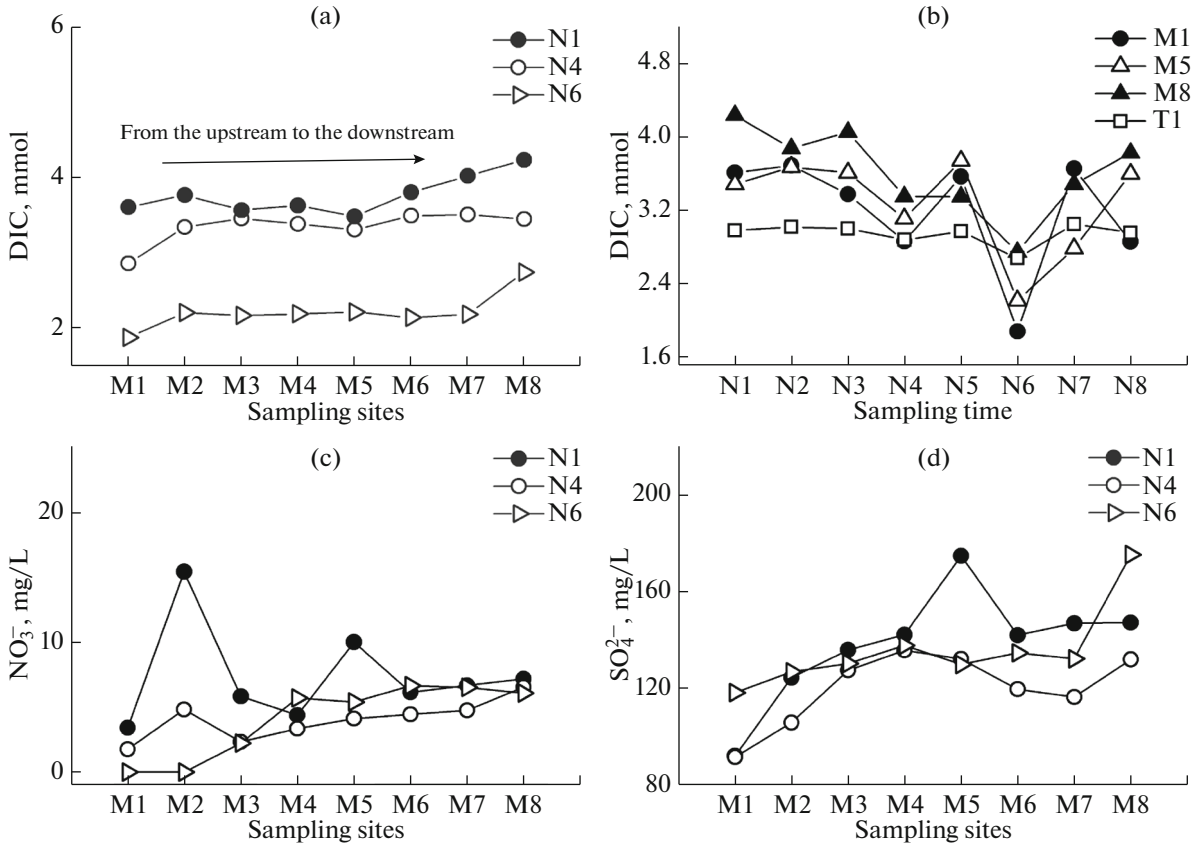

Fig. 4. (a) Spatial variations of DIC contents for N1, N4, and N6. (b) Temporal variations of DIC contents for M1, M5, M8, and T1. (c) Spatial variations of NO_3^- for N1, N4, and N6. d. Spatial variations of SO_4^{2-} for N1, N4, and N6.

the Nanming River. DIC in riverine water generally has three sources, atmospheric CO_2, CO_2 from organic respiration, and carbonate dissolution (Li et al., 2010). DIC sources can be represented using the following equations: (I) Dissolution of CO_2 (including soil and atmospheric CO_2) and reactions in water environment are an important source for DIC, soil CO_2 mainly from decay of organic matter and infiltration of atmospheric CO_2.

$$(CH_2O)_n + nO_2 \rightarrow nH_2O + nCO_2, \quad (2)$$

$$nCO_2 + H_2O \rightarrow H_2CO_3. \quad (3)$$

(II) Weathering of rocks (including carbonate and silicate bedrock) by acids (e.g., carbonic acid and sulfuric acid) is a main source of DIC. Li et al. (2008) have demonstrated that sulfuric acid significantly contributes to the chemical weathering of carbonate rocks in Guizhou Province, southwest China.

$$(Ca_{2-x}Mg_x)(CO_3)_2 + 2H_2CO_3 \rightarrow (2-x)Ca^{2+} + xMg^{2+} + 4HCO_3^-, \quad (4)$$

$$(Ca_{2-x}Mg_x)(CO_3)_2 + 2H_2SO_4 \rightarrow (2-x)Ca^{2+} + xMg^{2+} + 2HCO_3^- + SO_4^{2-}. \quad (5)$$

These processes not only vary temporally but also control the DIC dynamics in the aquatic system. The contribution of atmospheric CO_2 was minor because of the low concentration of alkalinity in the rain water. The main sources of DIC were from soil CO_2, decay of organic matters, and chemical weathering of rocks.

As indicated by Figs. 4c, 4d, it was found that the nitrate and sulfate increased significantly from M1 to M5 when the Nanming River flowed through urban area. Nitrate and sulfate contents in the most rain water samples were generally lower than 0.5 and 10 mg/L during sampling periods, respectively. The result was agreement with previous study in Guiyang City (Han and Liu, 2006), showing relative low nitrate and sulfate in rain water compared with those in river water. High contents of nitrate and sulfate in surface waters mainly originated from anthropogenic inputs (Lang et al., 2006). Thus, the results suggested significant anthropogenic pollution influenced on water quality in the Nanming river.

4.3.2. The shift of $\delta^{13}C_{DIC}$ values responding to hydrological events. The temporal and spatial variations of DIC shed the light on the behavior and sources of DIC in the riverine water. The $\delta^{13}C_{DIC}$ is a

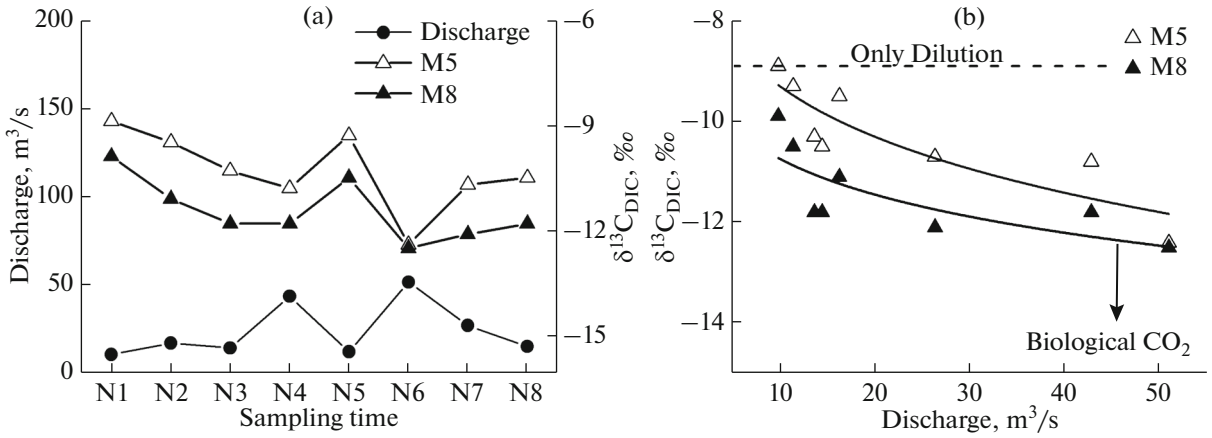

Fig. 5. Correlation between $\delta^{13}C_{DIC}$ and discharge at sites M5 and M8.

useful tracer of processes that dominate the carbon cycle in aquatic systems (Telmer and J., 1999; Hélie et al., 2002; Barth et al., 2003; Zhong et al., 2017). Before interpreting the variations of $\delta^{13}C_{DIC}$ values in the Nanming River, the $\delta^{13}C_{DIC}$ values for the source materials are shown as follows: The average $\delta^{13}C$ values of the carbonate rocks were reported to be near +1.8‰ in Guizhou province (Li et al., 2008), and the values of $\delta^{13}C_{DIC}$ for atmospheric CO_2 is about −8‰. Due to root respiration, oxidation of organic material, and bacterial respiration, the soil is considerably richer in CO_2 than the atmosphere (Telmer and J. 1999). The $\delta^{13}C$ of soil CO_2 depends on the source material (plant type) and the rate of diffusion. Li et al. (2010) have suggested that the $\delta^{13}C$ value of soil CO_2 is about −21‰ in the Guizhou Province of southwest China with C_3 plant coverage. The dissolution of soil CO_2 in soil water will then give soil water an average $\delta^{13}C$ of −17‰ (Wang et al., 2011). Based on the above end-member values, the possible contributions of the carbon can be estimated. Carbonate is widely distributed in the studied area, the $\delta^{13}C_{DIC}$ derived from carbonate dissolved by soil water CO_2 should be around −7.6‰, and the $\delta^{13}C_{DIC}$ value derived from carbonate dissolved by strong acid (e.g., nitric acid and sulfuric acid) should be close to +1.8‰. The values of $\delta^{13}C_{DIC}$ in riverine water ranged from −12.8 to −7.9‰, with a median value of −10.6‰, which is more negative than the values (−8.3‰) in 2002 (Lang et al., 2006), attributing to the intense anthropogenic inputs with the development of urbanization. The results showed that carbonate dissolved by soil CO_2 was the main source of DIC in the Nanming River, as equation (4). However, all of the $\delta^{13}C_{DIC}$ values were slightly below −7.6‰, which should be attributed to the decomposition of organic matter.

The temporal variations of $\delta^{13}C_{DIC}$ for the Nanming River with varied discharge were shown in Fig. 5a, and the riverine water after rain events was clearly enriched in ^{12}C, which suggested a large amount of ^{13}C-depleted biogenic carbon was involved with the influx of rain water. As seen in Fig. 5b, the $\delta^{13}C_{DIC}$ values exhibited a power-law mixture effect with increasing discharge, indicating that there was a power-law relationship between the $\delta^{13}C_{DIC}$ values and discharge. Acid rain emerged as an important environmental problem in southwestern China and there was a high SO_4^{2-} content and low pH values (Li et al., 2008). The rainwater scoured the land, with soil CO_2 and ions dissolved in the water, which then fluxed into the river. We analyzed the $\delta^{13}C_{DIC}$ values of running water on the road surface when it rained, the average value of which was −19.1‰. The flow velocity of the Nanming River was fast and few water plants were found in the river, so photosynthesis and respiration can be neglected during the monsoon season. The decomposition of organic matter occurred on land, and the DIC produced by the biological activities was flushed into the river when it rained. The $\delta^{13}C_{DIC}$ tended toward negative values after a rainstorm, possibly, due to dissolution of soil CO_2 and rainwater fluviraption (Zhong et al., 2017). The $\delta^{13}C_{DIC}$ of sewage in Guiyang city had an average value of −11.3‰, and the values of $\delta^{13}C_{DIC}$ in M5 were more positive than that in M8, which may be ascribed to the injection of sewage and the decay of organic matter along the river. The hydrological controls and anthropogenic inputs should be responsible for the variations of DIC dynamics in the monsoon season for an urban river.

4.3.3. The relation between DIC and $\delta^{13}C_{DIC}$. The DIC is related to the carbon isotopic evolution (Jiang, 2013), and the DIC that originated from the degradation of organic matter can shift the values of $\delta^{13}C_{DIC}$ towards negative values. The $\delta^{13}C_{DIC}$ values had a negative correlation with the DIC concentrations for the mainstream during different sampling campaigns

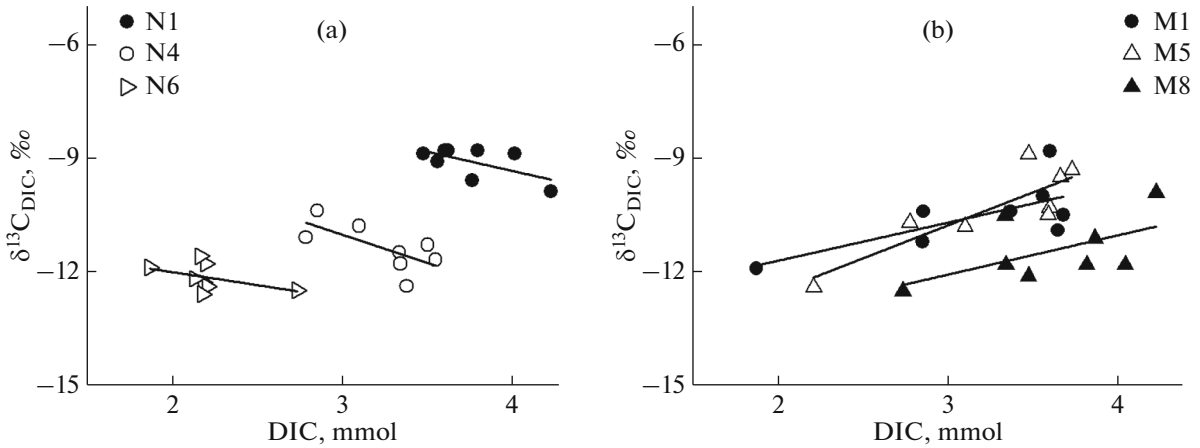

Fig. 6. (a) Linear regression of DIC contents and $\delta^{13}C_{DIC}$ values for N1, N2, and N3. (b) Linear regression of DIC contents and $\delta^{13}C_{DIC}$ values for M1, M5, and M8 respectively.

(Fig. 6a), indicating Eqs. (2), (3) would occur along the mainstream of the river. From the upstream to the downstream of Nanming River, a large amount of pollutants was poured into the river with increasing anthropogenic activities. The degradation of organic pollutants resulted in high DIC concentrations, which had relative negative $\delta^{13}C_{DIC}$ values. Figure 6b showed that the values of $\delta^{13}C_{DIC}$ had a positive correlation with the DIC concentrations for specific sampling sites. In response to the decreased DIC concentrations, relative negative $\delta^{13}C_{DIC}$ values were seen after rainstorms (Figs. 5 and 6b), likely due to the dilution of rainwater and influx of biological CO_2. There are many weathering processes affecting the DIC dynamics such as carbonate weathering by H_2CO_3, silicate weathering by H_2CO_3, carbonate weathering by H_2SO_4, soil CO_2 dissolution, degradation of organic matters and CO_2 degassing (Fig. 7). High content of SO_4^{2-} was found in the Nanming River. Urban inputs may be an important source for SO_4^{2-}. However, the effect of carbonate weathering by H_2SO_4 on DIC could be covered by the effect of anthropogenic inputs and biological CO_2 producing. Rainfall would enhance the soil water content available for biological respiration and soil CO_2 flux (Hélie et al., 2002; Barnes and Raymond, 2009; Li et al., 2010). The rainwater had low DIC concentrations for low pH values, so it was difficult to analyze these values of $\delta^{13}C_{DIC}$. The rainwater scoured the surface of the land, and the runoff water on the surface road had low DIC concentration (1.73 mmol/L) with negative $\delta^{13}C_{DIC}$ (−19.1‰) value, most of which were derived from the decomposition of organic matter and dissolution of soil CO_2. Low DIC concentrations and negative values of $\delta^{13}C_{DIC}$ were displayed with increased discharge for the riverine water after a rainstorm. Therefore, the decomposition of organic matter and the infiltration of soil CO_2 are some of the main factors controlling DIC behaviors and $\delta^{13}C_{DIC}$ compositions for an urban river during hydrological events.

4.4. Implications for Anthropogenic Activities

Human activity can greatly influence water chemistry, through waste and atmospheric input (Fan et al., 2014). Variation in total dissolved solutes in riverine water is not only related to drained basin lithology but also to land use and pollution from human activities (Gaillardet et al., 1999; Han and Liu 2004; Chetelat et al., 2008; Fan et al., 2014).

The dissolved solutes of anthropogenic inputs are generally different from that of natural sources, and higher values of dissolved solutes (such as Cl^-, SO_4^{2-},

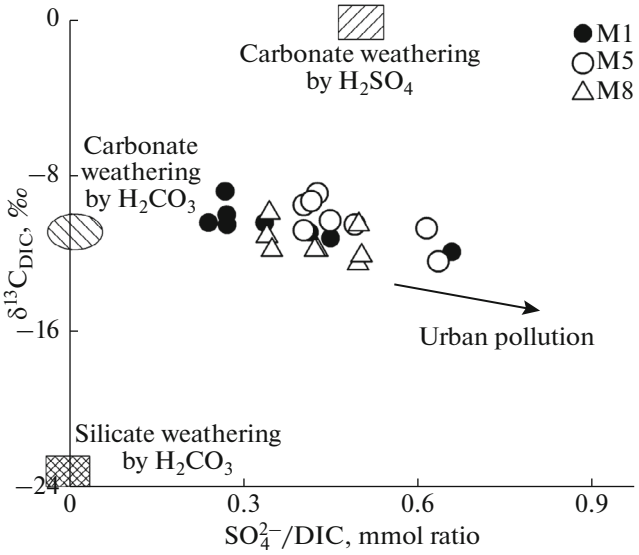

Fig. 7. Relationship between $\delta^{13}C_{DIC}$ versus SO_4^{2-}/DIC ratio.

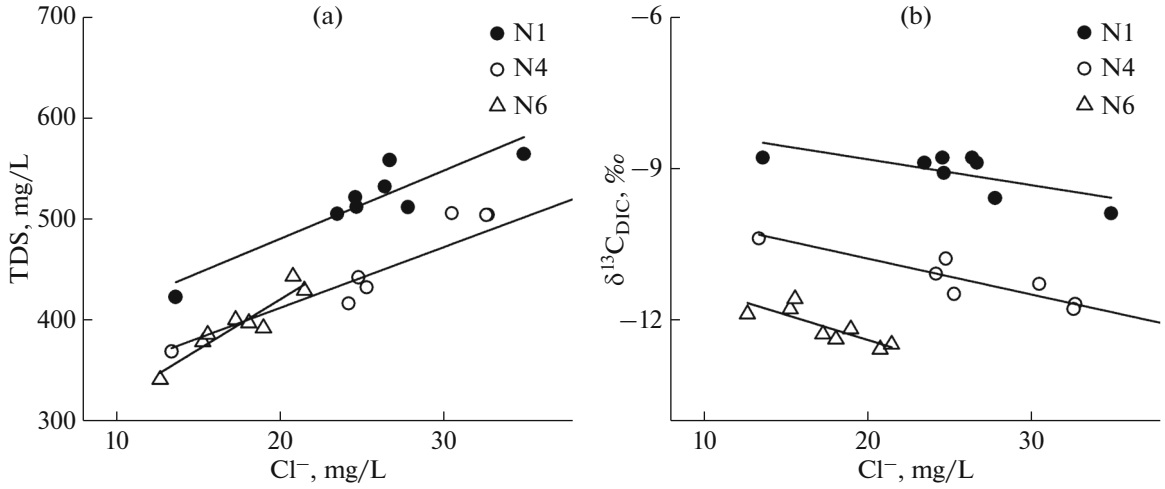

Fig. 8. (a) Plots showing variations of TDS vs. ($Cl^- + SO_4^{2-}$). (b) Showing variations of $\delta^{13}C_{DIC}$ vs. ($Cl^- + SO_4^{2-}$) for N1, N4, and N6, respectively.

NO_3^-, and DOC) are found in solutes derived from anthropogenic inputs than from natural sources. Nitrate, potassium, chloride, and sulfate are commonly considered sensitive to pollution (Fan et al., 2014). Cl^- showed more conservative behavior than other ions, and there are no other biogeochemical processes would occur in the urban area other than urban activities. The Cl^- may be derived from other sources such as the dissolution of halite and gypsum. However, we neglected the weathering of rock in the urban area due to the concrete protection along the Nanming River channels. The TDS values in the mainstream had a positive relation with Cl^- (Fig. 8a) along the mainstream for different sampling campaigns. These results suggested that anthropogenic inputs played an important role in these dissolved solutes, and the TDS was a useful indicator for pollution in an urban river, where other sources of major ions can be neglected.

A significant positive relation between $\delta^{13}C_{DIC}$ and Cl^- was found in the mainstream of Nanming River for the different sampling campaigns (Fig. 8b), reflecting that anthropogenic inputs shift the $\delta^{13}C_{DIC}$ values and indicating that $\delta^{13}C_{DIC}$ was a useful tracer to reflect the anthropogenic impacting. The relative negative values of $\delta^{13}C_{DIC}$ should be ascribed to the increasing decomposition of organic matter with increasing organic pollutant inputs in the urban area. The riverine water in the downstream showed higher Cl^- with more negative $\delta^{13}C_{DIC}$ values compared to upstream in the Nanming River, which suggested that the degradation of anthropogenic pollutants could shift the $\delta^{13}C_{DIC}$ toward negative values in the urban river. The $\delta^{13}C_{DIC}$ can be used to decipher the influence of human activities for an urban river.

5. CONCLUSIONS

This study showed spatial-temporal variations of dissolved solutes and variations of carbon dynamics responding to rainstorm events for an urban river in southwestern China. The TDS values and most of the major ion concentrations showed an increased trend from upstream to downstream, mainly, due to the effect of anthropogenic activities. And temporal variations showed that the TDS were diluted by rainwater after a rainstorm. In general, major ion constituents increased from upstream to downstream. However, due to precipitation, Mg^{2+}, Ca^{2+}, and HCO_3^- variations were not as insignificant as other ions with increasing anthropogenic inputs. HCO_3^- and SO_4^{2-} were dominant in the anions, and varied from 71.98 to 92.46%. Ca was dominant in the cations, accounting for 53.1% of all the cations. Most of the ions and TDS tended to follow a dilution effect, but the dilution effect did not strictly follow the theoretical dilution curve. Spatial variation of water chemistry suggested that anthropogenic inputs contributed significant solute load to the Nanming River, such as NO_3^- and SO_4^{2-}.

The DIC contents increased along the mainstream, and DIC was affected by the dilution effect. More negative $\delta^{13}C_{DIC}$ values were observed after a rainstorm, which may be related to the influx of water with biological CO_2. The $\delta^{13}C_{DIC}$ values had a negative relation with the DIC concentrations in the mainstream at different sampling campaigns, reflecting degradation of organic matter in the riverine channels. The spatial variations of $\delta^{13}C_{DIC}$ values had a positive relation with the DIC contents at specific sampling sites, suggesting the dilution effect and DIC with the negative $\delta^{13}C_{DIC}$ contribution during rain events. The

$\delta^{13}C_{DIC}$ and hydrochemistry indicated $\delta^{13}C_{DIC}$ is a useful tracer for natural and anthropogenic influences on water quality. This study suggested that hydrochemistry and $\delta^{13}C_{DIC}$ had a large variation responding to rainstorm events and anthropogenic impacts in the urban river. The results in this study indicated that urban pollution control and management need to be improved for protection of natural river eco-environment in the urban area at China.

ACKNOWLEDGMENTS

This work is financially supported by National Natural Science Foundation of China (Grant nos. 41173021 and 41422303), the Ministry of Science and Technology of China through Grant nos. 2013CB956700 and Water project of MEP (2012ZX07503003001).

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