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Temporal and Spatial Variations in Carbon/Nitrogen Output in the Karst Critical Zone and Its Response to the Forest Ecosystem of Karst Desertification Control

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Abstract: Rocky desertification is a common phenomenon in karst areas. Soil carbon and nitrogen storage is of great significance to the formation and evolution of ecosystems. Soil leakage is one of the important indicators in evaluating ecosystem stability. There are few studies on the response of carbon and nitrogen leakage below the surface of karst critical zones to forest ecosystems. The karst springs in the study area of Shibing Heichong, Bijie Salaxi and Guanling-Zhenfeng Huajiang in Guizhou, China, were selected to determine the variation characteristics of carbon and nitrogen content and karst spring outputs and their response to soil leakage. The results showed the following: (1) The content and output of carbon and nitrogen in karst springs in the three study areas showed obvious spatial differences. The carbon and nitrogen output of karst spring water was mainly concentrated in the rainy season. The carbon and nitrogen contents and output of karst springs in the Shibing Heichong study area were higher than those in the Bijie Salaxi and Guanling-Zhenfeng Huajiang study areas. (2) The carbon and nitrogen outputs of karst springs were mainly affected by flow. Land cover and land use in forests affect the carbon and nitrogen contents of karst springs and thus affect the output. (3) The higher the soil leakage of the karst spring was, the higher the carbon and nitrogen output. The leakage of the overlying soil in the Shibing Heichong study area was high, but the soil decline was small, and the stability of the forest ecosystem was relatively good. In summary, a lower degree of rocky desertification results in higher leakage from karst springs and higher risks of soil leakage; however, the ecosystem was relatively stable. Evaluating forest soil carbon and nitrogen loss and ecosystem stability in karst areas through the nutrient output of karst springs is of great significance for the prevention and control of rocky desertification areas.

Keywords: karst spring; soil; dissolved organic carbon/nitrogen; rocky desertification; terrestrial ecosystem

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1. Introduction

Earth's critical zone refers to a heterogeneous near-surface environment that vertically covers various spheres, including plant canopies, soil layers, air envelopes and aquifers, and is a key area for human survival and the functioning of Earth's ecosystems [1,2]. The Earth's critical zone is at the intersection of the atmosphere, biosphere, lithosphere, soil sphere and hydrosphere. The input of solar energy, as well as atmospheric processes and their gases and sediments, interact with biota, soil and rocks to provide ecosystem services. The hydrosphere cannot be divided as precisely as other spheres, and the hydrological cycle connects every link in the Earth's critical zone [1,3]. The hydrological cycle is also accompanied by material and energy transfer [2]. Approximately 10 to 15% of the Earth's land is covered by karst landforms, which are home to a quarter of the world's population [4]. The karst region of Southwest China, with the karst plateau of Guizhou as the centre, covers an area of more than 550,000 km^2 and is one of the three major continuous karst regions in the world. It is in the subtropical monsoon climate zone and has sufficient hydrothermal conditions and geological conditions, making this area the most complex, typical and diverse karst region in tropical and subtropical karst development in China and even the world [5]. Due to the extremely fragile karst ecological environment and unsustainable human activities in the local area, soil erosion is serious, resulting in bare surface bedrock and a poor rocky desertification environment. Critical zones of the earth control the surface ecological environment, change the surface morphology and stabilize life resources mainly through the process of rock weathering and soil formation. The karst critical zone is a type of critical zone developed against the background of carbonate rocks. The karst critical zone has the characteristics of a fast rock weathering rate and a slow soil formation rate [6], which are different from other areas. Its ecological environment is fragile, material energy exchange is frequent, and ecological and biogeochemical processes are extremely sensitive to climate change [7].

The year 2015 was the International Year of Soil, indicating the global importance of soil in ecosystem sustainability [8]. Soil not only facilitates many ecological processes but is also an important component of terrestrial ecosystems. Carbon and nitrogen storage in the soil is also very important for terrestrial ecosystems. Soil nitrogen storage is closely related to soil organic carbon storage [9,10]. Nitrogen deficiency affects plant growth and forest ecosystem stability [11,12]. Soil carbon and nitrogen content is affected by the dynamic balance of input and output [13], as well as the quantity and quality of litter, microorganisms and environmental factors [14–17]. The unique geological background and hydrological process in karst areas create a fragile ecosystem that is sensitive to human disturbance [18–20]. Different land use patterns will affect the soil carbon and nitrogen contents in forests. Compared with non-karst areas, forest ecosystems in karst areas are more sensitive. Different land use patterns have an impact on the basin, and deforestation increases the concentration and flux of dissolved organic carbon in surface water [21,22]. Previous research has demonstrated that soil C:N and tree species have a considerable influence on nitrogen release in forest watersheds [23]. The hydrological process of forest ecosystems includes the hydrological regulation process of the forest canopy, litter layer and soil layer [24]. Litter is a participant in the nutrient and hydrological cycle of forest ecosystems [25,26]. Spring water serves as an outlet for underground forest catchments and is used to monitor groundwater and interflow-related processes in headwaters and material flows in biogeochemical cycles [27]. Karst springs are the final manifestation of the results of groundwater lithospheric circulation in karst critical zones [28]. In karst regions, karst stores CO_2 in the atmosphere and soil as dissolved inorganic carbon (DIC) in karst water bodies [29]. Dissolved organic carbon (DOC) is not only an important component of organic carbon in water bodies but also an important component of the activated carbon pool in karst ecosystems [30,31]. Until now, research on carbon and nitrogen in water bodies has mainly focused on aquatic ecosystems. DOC is particularly important for organisms in water bodies and is the main source of energy [32]. While carbon and nitrogen in water are affected by organisms, environmental factors such as overlying vegetation, land use topography and hydrology will also affect the source, nature, distribution and migration of carbon and nitrogen in water bodies. Karst spring water is an important node of the carbon and nitrogen cycle and the output port of nutrient leakage, and it is also a typical medium for analysing the process and mechanism of the key carbon and nitrogen cycle of karst. The spring water in the karst key zone's central part was used to study the carbon and nitrogen output law and its influencing factors, as well as to reveal the relationship between carbon and nitrogen nutrient output and soil leakage in the forest ecosystem of rocky desertification control.

Karst desertification areas in southern China face serious problems such as soil erosion, soil nutrient loss and water scarcity. In the mountainous area of the Guizhou Plateau, which is representative of the overall structure of the karst ecological environment type in the south, Guanling-Zhenfeng Huajiang, Bijie Salaxi and Shibing Heichong were selected as the research areas. In this study, the carbon and nitrogen contents of karst spring water and overlying soil in the forests of the three study areas are assessed. The main objectives of this study are as follows: (1) to understand the variation characteristics of carbon and nitrogen content and output of karst spring water in this area, (2) to determine the factors influencing the carbon and nitrogen content and output in karst springs, and (3) to evaluate the response of karst spring water carbon and nitrogen output to surface forest ecosystems. This study can provide a scientific basis and theoretical support for karst underground leakage control and comprehensive management of rocky desertification.

2. Materials and Methods

2.1. Study Area

The selected demonstration areas are in the northwest and southwest of the Guizhou Plateau, and the karst landforms are widely developed and typical, representative of the landforms of plateau mountains, plateau canyons and mountain canyons of the karst plateau. The Bijie Salaxi Demonstration Area belongs to the karst plateau mountainous potential-mild rocky desertification area, and the Guanling-Zhenfeng Huajiang demonstration area belongs to the medium-intensity rocky desertification area of the karst plateau canyon and the no-potential rocky desertification area of the Shibing Heichong karst mountain canyon, which is typical of rocky desertification type areas in Guizhou and even the whole country (Figure 1).

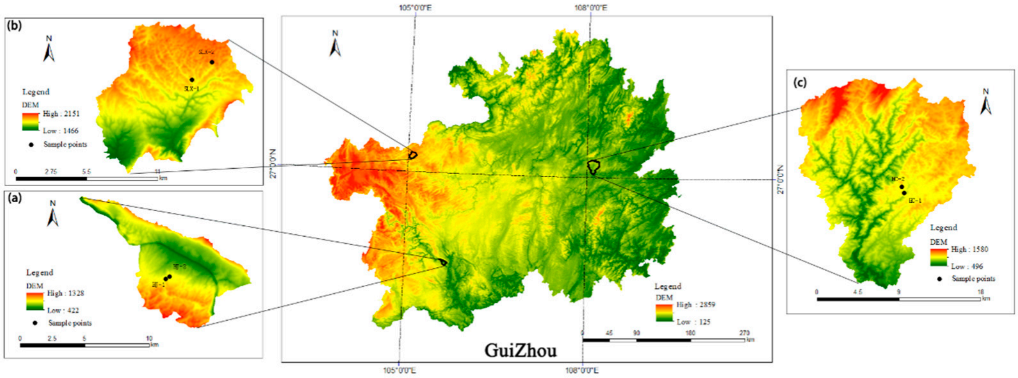


Figure 1. Overview of study area ((**a**) is Guanling-Zhenfeng Huajiang study area, (**b**) is Bijie Salaxi study area, (**c**) is Shibing Heichong study area).

The Guanling-Zhenfeng Huajiang Demonstration Area is a karst plateau canyon with an annual rainfall of 1052 mm, most of which forms surface runoff into the river; a small part enters groundwater, and the source of drinking and irrigation is mainly spring water. The rocky desertification control demonstration area of the Guanling-Zhenfeng Huajiang Plateau Canyon is in the slope area from the cattle farm basin to the Beipan River Gorge, and the Beipan River constitutes the erosion datum of the entire area. The lithology is mainly Middle and Upper Triassic limestone and grey matter dolomite, the soil erosion problem is serious, and the rocky desertification grade is primarily medium and intense. The Bijie Salaxi demonstration area belongs to the karst plateau mountainous area and has a potential-mild rocky desertification grade, with an annual rainfall of 984 mm and a lack of water resources. In terms of geology and geomorphology, the Bijie Salaxi Plateau Mountain Rocky Desertification Control Demonstration Area is in the upper reaches of the Wujiang River Basin in the transition slope zone from the Eastern Yunnan Plateau to the Qianzhong Mountain Plain Hills, with large undulating terrain, mainly peaks, troughs and hilly depressions. The outcropping rock layer is mainly the middle and thick limestone of the Lower Permian, the groundwater level is shallow, and the soil is primarily limestone. Shibing Karst Plateau trough valley no-potential rocky desertification area, annual rainfall of 1130 mm, sufficient water resources, high utilization rate of water resources, agriculture and tourism developed. The Shibing Karst Demonstration Area is in northern Shibing County, Guizhou Province, on the slope of the transition from the Qianzhong Mountains to Xiangxi Hills, which belongs to a typical dolomite karst and has typical and complete geomorphological development.

The lithology of HJ-1 and HJ-2 in the Guanling-Zhenfeng Huajiang study area is mainly dolomite limestone, with a high exposure rate of surrounding rocks and low vegetation coverage. There are sparse low shrubs on both sides of HJ-1, and pepper is planted. The overlying land is primarily used for corn planting, and the spring area is 0.05 km^2. HJ-2 is surrounded by herbs, with the left and right sides of the pepper forest, thin and very little overlying soil, scattered tall shrubs, and a spring area of 0.06 km^2. The lithology of SLX-1 and SLX-2 in the Bijie Salaxi study area is limestone. SLX-1 is located at the foot of the mountain, surrounded by herbaceous plants, and covered with tall shrubs, and the secondary vegetation on the slope is mainly secondary vegetation. The closer to the steep slope, the higher the rock exposure rate, and the spring area is 0.08 km^2. SLX-2 is located at the bottom of the depression at the foot of the mountain. The overlying vegetation is mainly grass and shrub, with a small amount of exposed rock, surrounding depressions or slopes, and the spring area is 0.11 km^2. The lithology of HC-1 and HC-2 in the Shibing Heichong study area is dolomite. HC-1 is in the depression, and pine forests are distributed in the surrounding mountains. The overlying land is mainly used for planting tobacco, and there is a small area of artificially planted peach trees. The spring area is 0.12 km^2; HC-2 is surrounded by farmland, mainly rice farms, and the overlying land is also planted with corn. The spring area is 0.13 km^2.

2.2. Sample Collection and Preparation

2.2.1. Sampling and Pre-Treatment

From July 2020 to June 2021, karst spring water samples were collected and monitored monthly. A 100 mL polyethylene bottle, nitric acid and mercuric chloride solution were used for water sample collection and flow monitoring. Spring water samples were collected, a 100 mL polyethylene bottle was used to test soluble organic carbon, and a 100 mL polyethylene bottle was used for TN and NO_3-N. Each sample was collected and covered with a sealing film, sealed with Parafilm, and stored at 4 °C. Water level meters (HOBO U20, Onset, Bourne, MA, USA) were installed near karst springs. The monitoring frequency of the recorder was 30 min/time, and the runoff was monitored by the water level metre. The overlying soil of karst spring water under different rocky desertification conditions was collected in the rainy season and dry season. According to the principle of uniform distribution and representativeness, three soil profiles were selected in the overlying environment of spring water for soil collection. Before sampling, 1 kg of chemical soil was collected to determine the chemical properties of soil soluble organic carbon and nitrate nitrogen, with litterfall removed. The depth of soil collection in the Guanling-Zhenfeng Huajiang study area was 0 to 15 cm, the depth of soil collection in the Bijie Salaxi study area was 0 to 25 cm, and the depth of soil collection in the Shibing Heichong study area was 0 to 30 cm.

2.2.2. Laboratory Analysis

In the process of field sample collection, a HQ40d portable water quality analyser (HACH, Loveland, CO, USA) was used to test water temperature, pH and conductivity, and an alkalinity metre (Merck, Darmstadt, Germany) was used to titrate HCO_3^- on site and record. The soil samples were dried at 60 °C for 48 h, passed through a 0.25 mm sieve, and acidified with 1 mol L^{-1} HCl for analysis of soil soluble organic carbon. The sieved soil sample was added to super pure water, shaken and centrifuged for NO_3-N analysis. The water samples were filtered and tested for nitrate nitrogen and total nitrogen by a flow analyser (SYSTEA, Zona Industriale Paduni-Selciatella, Italy). DOC was measured using a TOC analyser (multi N/C 3100, Analytik Jena, Jena, Germany).

2.3. Data Analysis

2.3.1. Estimation of Carbon and Nitrogen Output from Karst Springs [33]

The monthly soluble organic carbon output ($\mathrm{F}i_{DOC}$) was calculated as follows:

$$\mathrm{F}i_{DOC} = \mathrm{C}i_{DOC} \times \mathrm{Q}i \times \mathrm{D}i \times 24 \times 60 \times 60 \quad (1)$$

where $\mathrm{C}i_{DOC}$ is the *i*-month carbon-nitrogen output (mg), C*i* is the *i*-month carbon-nitrogen content (mg L^{-1}), Q*i* is the *i*-month flow rate (mL/s), and D*i* is the *i*-month number of days (d). The monthly output of DIC, TN, and $\mathrm{NO_3}$-N was calculated in the same way.

In this study, the total one-year carbon and nitrogen output Fs_{DOC} was determined as follows:

$$\mathrm{Fs}_{DOC} = \sum_{i=1}^{n} \mathrm{F}i_{DOC} \quad (2)$$

where $\mathrm{F}i_{DOC}$ represents the monthly soluble organic carbon output (mg). The annual output of DIC, TN, and $\mathrm{NO_3}$-N was calculated in the same way.

2.3.2. Soil Carbon and Nitrogen Stocks [34]

The soil carbon and nitrogen density (DOCD) of each layer was calculated as follows:

$$\mathrm{DOCD}i = \mathrm{DOC}i \times \mathrm{B} \times \mathrm{D}i \times 10^{-2} \quad (3)$$

where DOCD*i* is the organic carbon density of layer *i* ($\mathrm{kg/m^2}$), DOC*i* is the soluble organic carbon content of layer *i* (g/kg), bulk density ($\mathrm{g/cm^3}$), and D*i* is the depth of layer *i* (cm). The $\mathrm{NO_3}$-N density ($\mathrm{DNO_3}$-N) was calculated in the same way

In this study, the total DOCS determination method of the spring area was as follows:

$$\mathrm{DOCS} = \sum_{i=1}^{n} \mathrm{DOCD}i \times \mathrm{S}i \quad (4)$$

where DOCS represents the total soluble organic carbon storage of soil in the plot (kg C), DOCD*i* represents the soluble organic carbon density of layer I ($\mathrm{kg/m^2}$), and S*i* represents the soil area ($\mathrm{m^2}$). $\mathrm{NO_3}$-N RESERVES ($\mathrm{NO_3}$-NS) were calculated in the same way.

2.4. Statistical Analysis

Excel 2019 (Microsoft Corporation, Albuquerque, NM, USA) was used to complete the statistical analysis. Origin2021b for drawing (OriginLab, Northampton, MA, USA) and Origin2021b were used for correlation analysis plotting. Statistical significance was defined as $p < 0.05$, and Spearman correlation analysis was used to determine the relationship between carbon and nitrogen output and carbon and nitrogen content, flow rate and water physical and chemical parameters. The study area was mapped using ArcGIS 10.7 (ESRI, RedLands, CA, USA).

3. Results

3.1. Carbon and Nitrogen Content and Category of Karst Spring Water

The DIC of HC-2 reached a maximum of 474 mg/L in November. That of SLX-2 reached a minimum of 174 mg/L in December. The DIC concentration in the karst spring water in the Shibing Heichong study area was 300~474 mg/L, which was significantly higher than that in the Guanling-Zhenfeng Huajiang study area and the Bijie Salaxi study area (Figure 2). The dissolved organic carbon (DOC) of HJ-2 reached a maximum value of 5.11 mg/L in October. The DOC of SLX-2 reached a minimum value of 1.60 mg/L in June. The concentration of DOC in the spring water in the Guanling-Zhenfeng Huajiang study area ranged from 2.01 to 5.11 mg L^{-1}, which was higher than that in the Bijie Salaxi study area and Shibing Heichong study area. The total nitrogen (TN) of HJ-1 reached a maximum value of 3.19 mg/L in October. The TN of HJ-2 reached a minimum value of 0.35 mg/L in November. The nitrate nitrogen (NO_3-N) reached a maximum value of 2.38 mg/L in April. The NO_3-N of HJ-2 reached a minimum value of 0.33 mg/L in September. The concentrations of TN and NO_3-N in spring water in the Shibingheichong study area were 1.15–2.65 mg/L and 1.12–2.38 mg/L, respectively, which were significantly higher than those in the Guanling-Zhenfeng Huajiang study area and Bijie Salaxi study area. The carbon and nitrogen contents of the spring water in the study area of the Guanling-Zhenfeng Huajiang River changed greatly, and the carbon and nitrogen contents of the spring water in the Bijie Salaxi study area changed slightly (Figure 2).

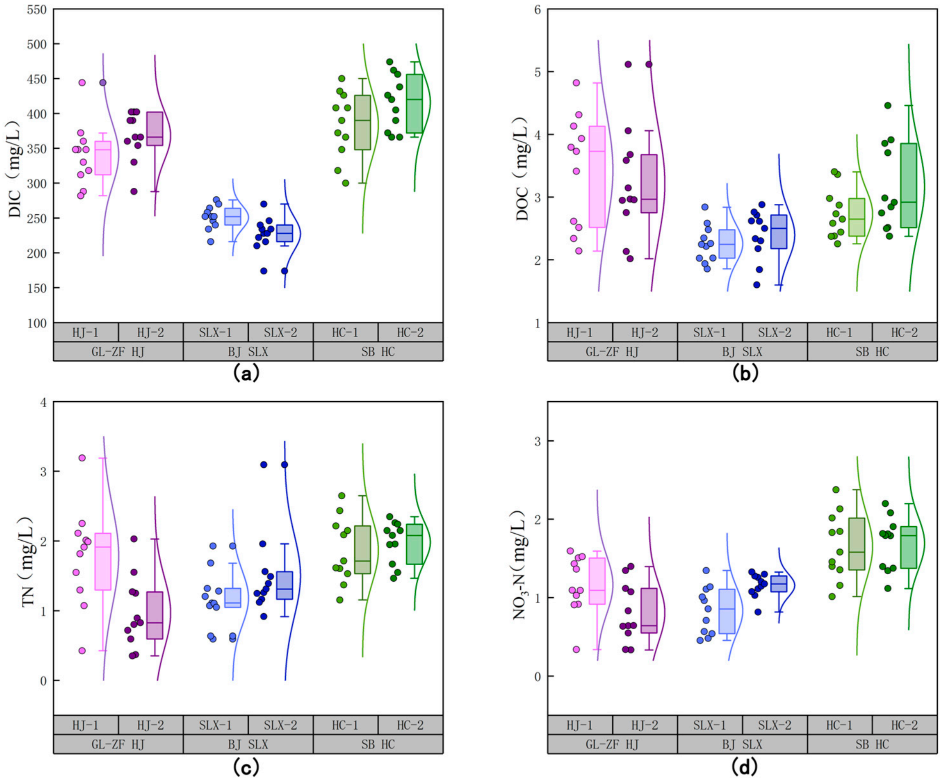


Figure 2. Comparison of DIC (**a**), DOC (**b**), TN (**c**) and NO_3-N (**d**) contents in karst spring water in the Guanling-Zhenfeng Huajiang Research Area, Bijie Salaxi Research Area and Shibing Heichong Research Area.

3.2. Flow Change Characteristics of Karst Springs

In the three study areas, the changes in karst spring flow showed obvious spatial and temporal differences (Figure 3). In the Guanling-Zhenfeng Huajiang study area, the overall flow rate of spring water was small, ranging from 11.15 mL/s to 101.63 mL/s, and the variation was small. The HJ-1 flow (42.10 mL/s) was slightly smaller than that of HJ-2 (45.72 mL/s), exhibited an upwards trend from July to October and from March to June, and stopped during the dry season. In the study area of Bijie Salaxi, the overall flow rate of spring water was 20.64 mL/s to 313.20 mL/s. The SLX-2 flow (154.16 mL/s) was larger than that of SLX-1 (117.67 mL/s), showing a downwards trend from July to August, an upwards trend from August to September and April to June, and a discontinuous trend in November, January and February during the dry season. In the Shibing Heichong study area, the overall flow rate of spring water was 13.08 to 527.03 mL/s, with a large variation. The HC-1 flow (131.24 mL/s) was slightly smaller than that of HC-2 (237.23 mL/s), showing a downwards trend from May to June, July to August, and September to January, an upwards trend from August to September and March to May, and a discontinuous trend in February during the dry season. In one hydrological year, the measured flow of karst springs was 43.91 mL/s (average) in the Guanling-Zhenfeng Huajiang study area, 135.92 mL/s (average) in the Bijie Salaxi study area, and 184.23 mL/s (average) in the Shibing Heichong study area.

From the measured flow rate, the monthly flow rate varied greatly; the maximum monthly flow was 527.03 mL/s (Shibing Heichong Research Area), and the minimum monthly flow was 11.15 mL/s (Guanling-Zhenfeng Huajiang Research Area). The monthly flow of karst springs in the Shibing Heichong Research Area was large, and the interruption time was short, while the monthly flow of karst springs in the Guanling-Zhenfeng Huajiang Research Area was small, and the interruption time was long. Atmospheric precipitation is the main source of groundwater recharge in spring basins [35,36]. In the three study areas, rainfall decreased at different times, and flow also decreased rapidly. The results showed that the trends of rainfall and flow were consistent (Figure 3). From April to June, the rainfall in the Bijie Salaxi study area increased from 84.8 mm to 234.60 mm, and the flow rates of SLX-1 and SLX-2 increased rapidly. The same phenomenon was observed in other study areas, indicating that the dynamic change in flow was sensitive to atmospheric precipitation.

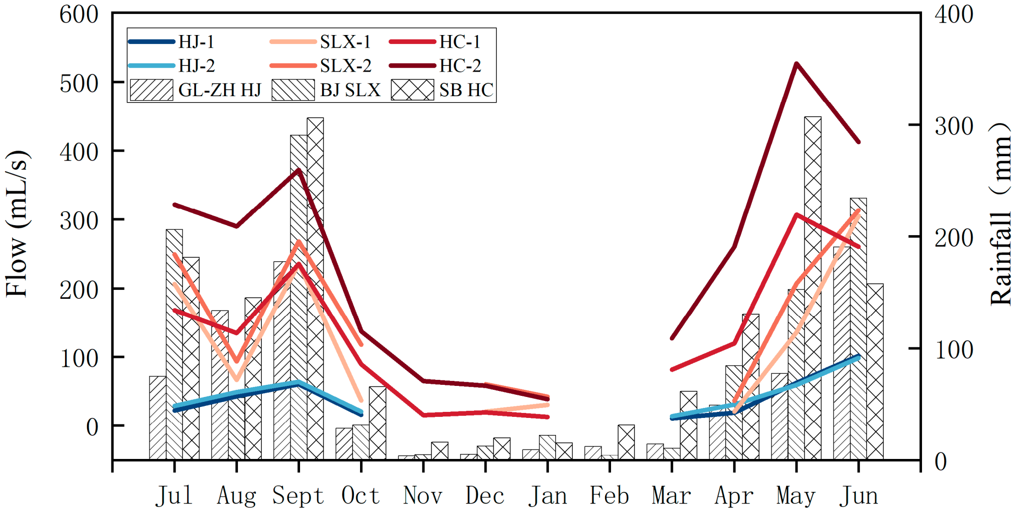


Figure 3. Trends of karst spring flow and rainfall.

3.3. Carbon and Nitrogen Contents in the Overlying Soil of Karst Springs

The contents of DOC and soil nitrate nitrogen (NO_3-N) in the overlying soil of the six karst springs showed a clear vertical change trend, that is, the surface layer > middle layer > lower layer (Figure 4). In the Guanling-Zhenfeng study area, the DOC content in the overlying soil of HJ-2 (9.76 mg/kg) was higher than that of HJ-1 (7.54 mg/kg), and the NO_3-N content was 7.13 mg/kg, which was less than that of HJ (7.96 mg/kg). The variation in the carbon and nitrogen contents in the soil of HJ-1 was greater than that of HJ-2. In the study area of Bijie Salaxi, the contents of DOC and NO_3-N in the overlying soil of SLX-2 were higher than those of SLX-1, and the change range was also greater than that of SLX-1. The contents of DOC and NO_3-N in the soil overlying HC-2 were higher than those of HC-1. In the three study areas, soil DOC and NO_3-N also showed obvious spatial characteristics, that is, Shibingheichong study area > Bijie Salaxi study area > Guanling-Zhenfenghuajiang study area. Additionally, the soil DOC content was higher in the dry season than in the rainy season. In the Guanling-Zhenfeng Huajiang research area and Shibing Heichong research area, the NO_3-N content in the overlying soil of the karst spring was higher in the rainy season than in the dry season (Figure 4).

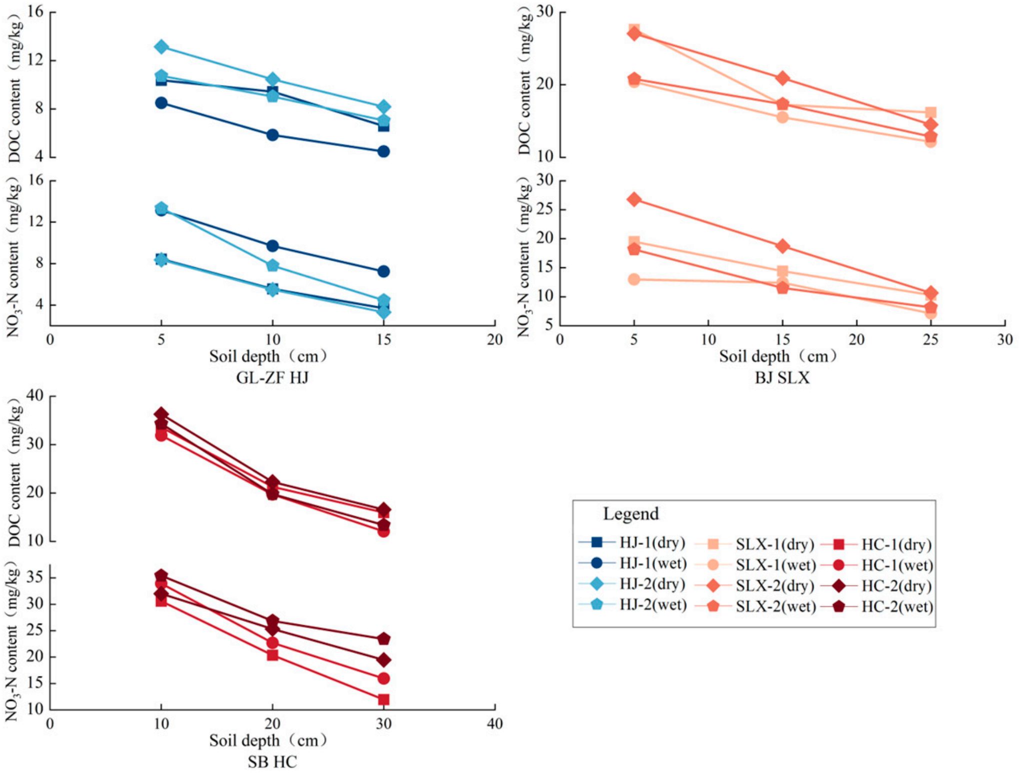
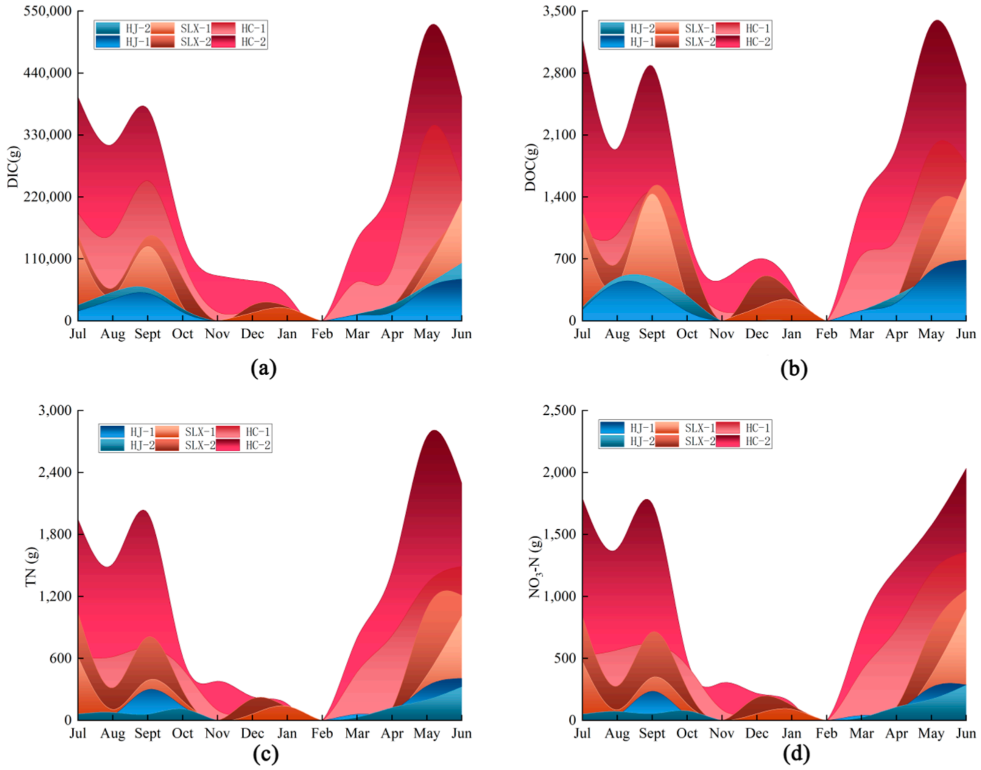


Figure 4. Comparison of DOC and NO_3-N contents in overlying soil of karst springs in Guanling-Zhenfeng Huajiang Research Area, Bijie Salaxi Research Area and Shibing Heichong Research Area.

3.4. Carbon and Nitrogen Output of Karst Springs

In the three study areas, the carbon and nitrogen outputs of karst spring water exhibited obvious spatial and temporal differences (Figure 5). The maximum monthly carbon and nitrogen output of karst springs occurs during the rainy season, and the output is also concentrated in summer and autumn. Karst spring water in the Bijie Salaxi Research Area accounted for the highest proportion of carbon and nitrogen output in summer and autumn at 71% to 80%. The maximum was reached in June 2021, with DOC fluxes of SLX-1 and SLX-2 of 1.60 kg and 1.30 kg, DIC fluxes of 213.47 kg and 189.96 kg, TN fluxes of 1.01 kg and 1.21 kg, and NO_3-N fluxes of 0.90 kg and 1.05 kg, respectively. The carbon and nitrogen outputs in the Guanling-Zhenfeng Huajiang Research Area and the Bijie Salaxi Research Area reached their highest values in June, and the carbon and nitrogen outputs in the Shibing Heichong Research Area reached their maximum values in May. The DOC fluxes of HC-1 and HC-2 were 1.79 kg and 2.67 kg, DIC fluxes were 246.68 kg and 397.61 kg, TN fluxes were 1.49 kg and 2.30 kg, and NO_3-N fluxes were 1.36 kg and 2.04 kg, respectively. During the dry season, the flow rate of karst springs continues to be low, and even the flow is interrupted to varying degrees, resulting in a low monthly output of carbon and nitrogen. In March of the dry season, the flow rate of HJ-2 (13.91 mL/s) in the Guanling-Zhenfeng Huajiang Study Area was slightly greater than that of HJ-1 (11.15 mL/s), but the nitrogen output of HJ-2 was slightly lower than that of HJ-1 because the nitrogen content of HJ-1 was higher than that of HJ-2. In this study, we observed that the seasonal variation characteristics of carbon and nitrogen fluxes in karst spring water were consistent with the research phenomenon of river flux in the Zhujiang River [37].



(a) **(b)** **(c)** **(d)**

Figure 5. Monthly carbon and nitrogen output of karst springs ((**a**) is DIC monthly output. (**b**) is DOC monthly output. (**c**) is TN monthly output. (**d**) is NO_3-N monthly output.)

4. Discussion

4.1. Influencing Factors of the Carbon and Nitrogen Outputs of Karst Spring Water

The carbon and nitrogen outputs of karst springs also exhibited obvious spatial characteristics. The annual output of carbon and nitrogen in Shibing Heichong spring water is 1.25 to 4.71 times that of the Bijie Salaxi research area and 3.46~14.25 times that of the Guanling-Zhenfeng Huajiang research area. In the above, the flow rate and carbon and nitrogen output showed obvious spatial characteristics. There was a significant correlation between carbon and nitrogen output and the flow rate of karst spring water ($p < 0.001$), indicating that the carbon and nitrogen output of karst spring water was mainly affected by the flow. Previous studies have also shown that differences in nutrient flux were mainly due to differences in flow [38]. The annual carbon and nitrogen output of spring water in the Bijie Salaxi Research Area was 1.89, which was 5.24 times that of spring water in the Guanling-Zhenfeng Huajiang Research Area. In the Guanling-Zhenfeng Huajiang study area, the HJ-2 flow rate (45.71 mL/s) was slightly greater than that of HJ-1 (42.10 mL/s). The annual output of DOC and DIC (2.84 kg/a, 368.04 kg/a) of HJ-2 was higher than that of HJ-1 (2.62 kg/a, 278.73 kg/a), while the annual output of TN and NO_3-N (0.99 kg/a, 0.84 kg/a) of HJ-2 was slightly lower than that of HJ-1 (1.44 kg/a, 1.05 kg/a). In the Guanling-Zhenfeng Huajiang study area, the difference in karst spring flow was small, and the nitrogen output of HJ-2 was lower than that of HJ-1 due to the influence of carbon and nitrogen content. As shown in Figure 6, there was a significant correlation between carbon and nitrogen content and output ($p < 0.01$), and the output was also affected by the content. The carbon and nitrogen output of karst springs is mainly affected by the flow rate, followed by the carbon and nitrogen content.

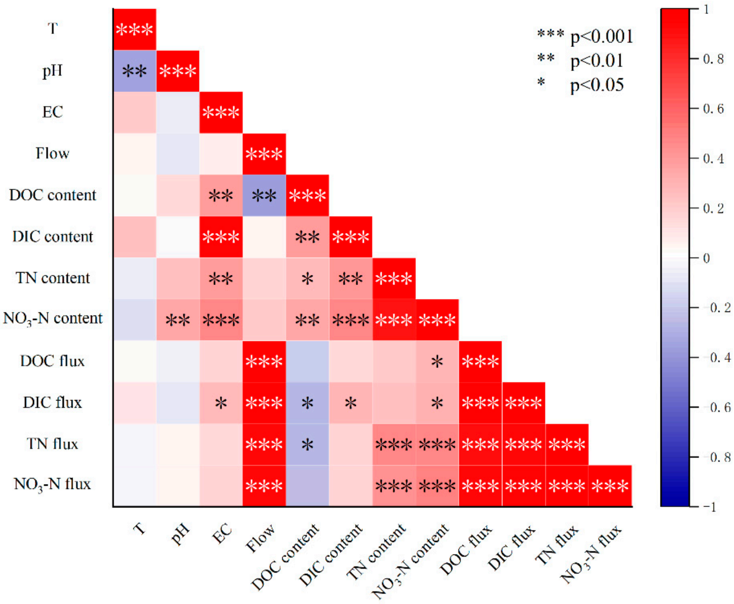


Figure 6. Spearman correlation coefficient of carbon and nitrogen output, carbon and nitrogen content and water chemical parameters in karst springs.

We found that karst spring water carbon and nitrogen output was mainly affected by the flow. The karst spring water in the three study areas had different degrees of disconnection. For the Shibing Heichong study area, the cut-off time was shorter, and the flow was much higher than that in the other two study areas. Thicker soil, higher vegetation coverage, soil cover and vegetation litter can also improve soil water retention and water storage capacity [39] and increase field water holding capacity and soil water content, which is conducive to the continuity of spring water flow. The Guanling-Zhenfeng Huajiang study area belongs to the karst plateau canyon with a steep slope (22°–30°), resulting in groundwater infiltration [40,41], and low vegetation coverage leads to poor rainfall interception [42]. Therefore, the karst spring water flow in the study area is 43.91 mL/s (mean), and the cut-off time is longer.

4.2. Influencing Factors of the Carbon and Nitrogen Contents of Karst Spring Water

The contents of DIC, TN and NO_3-N in the karst spring were much higher than those in the Guanling-Zhenfeng Huajiang study area and Bijie Salaxi study area. DIC in karst spring water is mainly composed of dissolved CO_2, H_2CO_3, HCO_3^- and CO_3^{2-} [43]. When the pH in the water body is between 6.35 and 9.33 and is weakly alkaline, the DIC in the water body is mainly HCO_3^- [44]. In field tests of spring water in the three study areas, CO_3^{2-} values were lower and free CO_2 content in the water was also small, so DIC levels in the study areas could be expressed by HCO_3^- concentrations. The concentration of DIC in karst spring water in the Shibing Heichong research area ranged from 300 to 474 mg/L, which was significantly higher than that in the Huajiang Research Area and Salaxi Research Area. DIC in karst areas is mainly affected by carbonate rocks, and the solubility of different carbonate rocks is also different. The lithology of the Shibing Heichong Research Area is dolomite, the lithology of the Bijie Salaxi Research Area is limestone, and the lithology of the Guanling-Zhenfeng Huajiang Research Area is grey dolomite [33,45]. The litter of vegetation in the Shibing-Heichong study area had relatively stable nutrient input [46–48], which maintained the stability of the soil carbon and nitrogen contents, so the soil carbon and nitrogen contents were significantly higher than those of the other study areas (Figure 4). The differences in the DOC, TN and NO_3-N contents in spring water in the Shibing Heichong study area were relatively small.

A higher degree of rocky desertification limits the growth of plants, resulting in a fragile ecosystem [49–51]. The vegetation and soil coverage in the Guanling-Zhenfeng

Huajiang study area of moderate-intensity rocky desertification were low. The vegetation types were mainly economic crops, corn, pepper, loquat seedlings, etc., and the planting mode was relatively simple. The ecosystem was relatively fragile, and the soil carbon and nitrogen contents were low. At the same time, farming leads to small and large differences in the carbon and nitrogen contents in spring water (Figure 2). Areas with low rocky desertification provide a better environment for vegetation survival and more plant species due to low degradation, and the species richness in these areas is higher than that in areas with high rocky desertification [52,53]. The study area of Bijie Salaxi in the Shibing Heichong study area belongs to the no-potential rocky desertification grade and potential-mild rocky desertification grade. The vegetation type and coverage rate were higher than those in the Guanling-Zhenfeng Huajiang study area, and the DOC content in soil was also relatively high. The concentration of DOC in spring water in the Guanling-Zhenfeng Huajiang study area ranged from 2.01 to 5.11 mg/L, which was higher than that in the Bijie Salaxi study area and Shibing Heichong study area. HJ-1 and HJ-2 contained a large number of phytoplankton and bacteria, and biological mechanisms such as phytoplankton and bacteria production are considered to be an important source of DOC [54], resulting in a higher DOC content. Different land-use patterns and vegetation cover affect the variation in the carbon and nitrogen contents in water [55–57]. The soil thickness of karst spring water in the Guanling-Zhenfeng Huajiang research area was thin, the vegetation coverage was low, and it was agricultural land, which is affected by agricultural farming. The carbon and nitrogen contents of spring water in the Guanling-Zhenfeng Huajiang research area more were concentrated than those in the other research areas, and the change range was large (Figure 2). The contents of carbon and nitrogen in karst springs in the study area of Salaxi Spring in Bijie were relatively concentrated, and the change range was small because the water cover vegetation is mainly secondary vegetation and is not affected by human activities.

4.3. Response of Karst Spring Water Carbon and Nitrogen Output to the Surface Ecosystem

Karst is a typical ecologically fragile area. Soil carbon and nitrogen storage is key to the formation and evolution of local ecosystems. As the most active components of soil carbon and nitrogen [58–61], soluble carbon and nitrogen are extremely sensitive to environmental changes. Water resources carry nutrients into groundwater through soil circulation [3,8]. The aboveground-underground dual hydrological structure in karst areas leads to the characteristics of aboveground-underground double loss of nutrients. Spring water is an important output port of forest groundwater [3,62,63] and plays a very important role in underground leakage in karst areas.

When comparing carbon and nitrogen storage, we found that the DOC storage in the dry season was significantly higher than that in the rainy season (Figure 7), which was consistent with the results of other studies on carbon storage [60,61]. The NO_3-N storage in the Shibing Heichong study area and the Guanling-Zhenfeng Huajiang study area was greater in the wet season than in the dry season. This is because the soil NO_3-N storage increased in the rainy season due to the influence of agricultural fertilization. Agricultural activities seriously affect soil nitrogen content and storage and decrease the stability of soil organic matter [64,65]. In contrast, in the Bijie Salaxi research area, the karst spring was not affected by agriculture, and the NO_3-N reserves in the dry season were greater than those in the rainy season. We observed significant differences in karst springs and carbon and nitrogen outputs with different carbon and nitrogen reserves. Due to land use/cover change, there are significant differences in soil carbon and nitrogen storage [66–68]. The vegetation and soil cover rate of the study area was as high as >50%, which was higher than that of the Bijie Salaxi study area (30%~50%) and Guanling-Zhenfeng Huajiang study area (10%~35%) [33]. The carbon and nitrogen storage in the Shibing Heichong study area was significantly higher than that in the Bijie Salaxi study area and the Guanling-Zhenfeng Huajiang study area (Figure 7). As shown in the figure, the carbon and nitrogen reserves of the spring area in the Bijie Salaxi study area were 2.33 to 10.64 times those of the

Guanling-Zhenfeng Huajiang study area. In the above analysis, karst spring water carbon and nitrogen output measurements were in the following order: Shibing Heichong study area > Bijie Salaxi study area > Guanling-Zhenfeng Huajiang study area. In the study area of Shibing Heichong, the carbon and nitrogen storage of HC-2 spring was greater than that of HC-1, and the carbon and nitrogen output of HC-2 karst spring was also greater than that of HC-1. The Bijie Salaxi area and Guanling-Zhenfeng Huajiang study area also exhibited the same phenomenon. The results showed that the higher the carbon and nitrogen storage in the karst spring area was, the higher the carbon and nitrogen output of the karst spring. Comparing the annual output and soil leakage of six karst springs, we found that the DOC leakage and output in the HC-2 spring area were the largest, which were 136.75 kg and 19.94 kg, respectively. In the Guanling-Zhenfeng Huajiang study area, the DOC output of HJ-2 spring water was slightly larger than that of HJ-1. The difference in DOC reserves in HJ-1 is 23.91 kg, which was greater than that of 18.24 kg in the HJ-2 spring area. The increase in NO_3-N storage in the HJ-1 spring area was higher than that in the HJ-2 spring area, indicating that HJ-1 was more affected by agriculture, resulting in more serious soil leakage [69–71]. The overlying soil environment of different karst springs has different carbon and nitrogen reserves. Due to the continuous supply of soil with high carbon and nitrogen contents, the annual output of carbon and nitrogen in karst spring water is relatively high, resulting in relatively high soil nutrient leakage. Due to the continuous supply of low-carbon nitrogen content soil, the annual output of carbon and nitrogen in karst spring water is relatively low, and the resulting soil nutrient leakage is also relatively low.

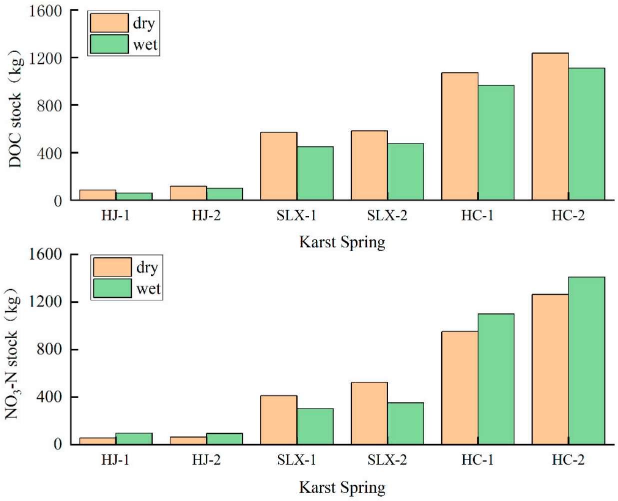


Figure 7. Comparison of DOC and NO_3-N storage in overlying soil of karst spring.

Stability refers to the ability of ecosystems to maintain and restore their own functions and structures, representing the reliability of ecosystems to provide normal service functions [72,73]. Disturbance or disturbance refers to changes affecting ecosystems [74–76]. The response of ecosystems to disturbance is a multilevel and multiscale process. Evaluating ecosystem stability is a way to quantify the response of a specific level and scale. Soil is the medium for storing a large amount of nutrients and is essential for plant growth. Therefore, the soil nutrient loss rate is an important indicator for evaluating ecosystem stability. It is concluded that greater carbon and nitrogen storage above the karst spring results in higher annual outputs of carbon and nitrogen in the spring and more soil nutrient leakage in the forest ecosystem. This result indicates that the risk of soil nutrient loss in areas with low rocky desertification grades is also higher than that in areas with high rocky desertification grades. In the study area of Shibing Heichong, the soil loss, karst spring water output and output rate were relatively high. At the same time, there are many types of vegetation and high coverage, and the nutrient input to the ecosystem through rich litter is stable and high [77,78]. The decline in soil carbon and nitrogen storage (leakage rate) in the Shibingheichong study area was far less than that in the other two study areas. In the Guanling-Zhenfeng Huajiang study area, soil loss, karst spring water output and output rate were relatively low, soil cover and vegetation cover were low, rocky desertification degree was high and nutrient input was low. The soil carbon and nitrogen storage in the Guanling-Zhenfeng Huajiang research area decreased greatly (leakage rate). The Bijie Salaxi study area was at an intermediate level.

5. Conclusions

In the three study areas, the carbon and nitrogen contents and output of karst springs showed obvious spatial and temporal variation characteristics. The contents of DIC, TN and NO_3-N in karst springs in the Shibing Heichong study area were significantly higher than those in the Bijie Salaxi study area and Guanling-Zhenfeng Huajiang study area. The DOC content of karst springs in the Guanling-Zhenfeng Huajiang study area was higher than that in the other two study areas. Karst spring carbon and nitrogen contents were affected by local lithology, land use, zooplankton and other factors. The output of carbon and nitrogen in karst springs was found to be in the following order: Shibing Heichong research area > Bijie Salaxi research area > Guanling-Zhenfeng Huajiang research area. Karst spring carbon and nitrogen output was mainly concentrated in the rainy season and was mainly affected by the flow, followed by carbon and nitrogen content. The carbon and nitrogen outputs of the karst spring were more sensitive to the response to rainfall.

The contents of carbon and nitrogen in the overlying soil of karst springs also showed temporal and spatial characteristics. No potential rocky desertification Shibing Heichong studied soil cover, vegetation coverage was high, and soil carbon and nitrogen contents were significant in the other two study areas. The DOC content in soil was affected by litter, and the DOC content in the dry season was greater than that in the rainy season. Affected by agriculture, the NO_3-N content in the soil of the Shibing Heichong study area and Guanling-Zhenfeng Huajiang study area was higher in the rainy season than in the dry season. The lower the carbon and nitrogen output of the karst spring in the Guanling-Zhenfeng Huajiang research area was, the lower the carbon and nitrogen leakage of the overlying soil. The carbon and nitrogen output of karst springs in the study area was higher, and the soil carbon and nitrogen leakage were also higher, but at the same time, the soil carbon and nitrogen input were also high, and the soil decline was low. This result shows that the overlying forest ecosystem of karst springs was relatively stable and had strong anti-interference in the Shibing Heichong research area. Karst springs play a vital role in the carbon and nitrogen cycles in the karst critical zone. This study can provide a scientific foundation and theoretical support for comprehensively studying forest water and soil nutrient loss in karst areas by examining the interannual change in carbon and nitrogen compounds in karst springs and soil.

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