Environ Geol (2009) 56:921–926
DOI 10.1007/s00254-008-1193-4

ORIGINAL ARTICLE

Hydrogeochemical effects of secondary forest in Guangxi Nongla karst areas in China

Xinhui Deng · Zhongcheng Jiang

Received: 24 December 2007 / Accepted: 7 January 2008 / Published online: 14 March 2008

Abstract Rainfall, throughfall, stemflow and spring were studied in a secondary forest during a wet season from April to August in 2006. Some of the chemicals in throughfall, stemflow and spring were increased in contrast with incident rainfall. Specifically, Cl^-, HCO_3^-, Na^+ and Ca^{2+} were leached negatively in throughfall, but K^+ and Mg^{2+} were leached positively. In stemflow, Cl^- and Na^+ were leached negatively, the others were leached positively and their concentrations were higher than those in throughfall. Total carbon, organic carbon and inorganic carbon in throughfall and stemflow were increased as rainfall went through the secondary forest. The concentration of free CO_2 in rainfall was lower than both, throughfall and stemflow; the relationship between total acidity and free CO_2 was linear. pH of throughfall and stemflow , such as maximum, minimum and mean, were lower than that of rainfall and the extent of pH in spring was changed minimally. We came to a conclusion that rainfall via the secondary forest can lead to further erosion, accelerate the biogeochemical cycle in epikarst zone, enhance the effective state of alkali elements in the soil, supply vegetation with more nutrients and advance vegetation's growth and succession, which are reasonably sufficient to form a stable karst ecosystem.

Keywords Rainfall · Throughfall · Stemflow · Spring · Subtropical secondary forest

X. Deng (✉)
Hunan University of Polytechnology,
412007 Zhuzhou, Hunan, China
e-mail: xhdeng2007@126.com

Z. Jiang
Institute of Karst Geology, CAGS,
541004 Guilin, Guangxi, China

Introduction

The ecologically fragile karst ecosystem is characterized by droughts, floods, soil erosion, rock desertification, surface collapse, limited biodiversity, low primary productivity, and poverty of human life (Yuan 1997). Vegetation is one of the important components in karst ecosystem. It is xerophile, calciphile, petrophile and sensitive to environmental changes. Karst processes can be controlled by the system CO_2–H_2O–$CaCO_3$, which is an open triphase disequilibrium system and also very sensitive to environmental change. In nature; this system couples with the carbon cycle, i.e., the CO_2–organic carbon–carbonate system (Yuan 1997).

In non-karst areas, intensive studies of chemical characteristics of rainfall, throughfall and stemflow in forest ecosystem have been carried out by Tian et al. (2002), Chen et al. (2004), Zhou et al. (2003), Pan et al. (1996), Chen et al. (2000), Roberto et al. (2001), Nelda and Noemi (2006), etc. In karst areas, some studies which focused on the relationship between preliminary karst forest and conservative water and soil (Ran et al. 2002) and on the chemical changes in rainwater after it has flown via the uncovered rock in karst areas (Jiang 1997), have been done. Researches on the changes in the chemical characteristics of bulk precipitation in water after it went through karst forest, which is very important not only to restore karst vegetation, rehabilitate water conservation forest and block rock desertification but also to further study karstic ecohydrological processes, are rare in karst areas.

This paper analyzed constituent fluxes and chemical characteristics of rainfall, throughfall, stemflow and epikarst spring in a subtropical secondary forest during a wet season from April to August 2006. The aim was to analyze the changes that occur in the chemical compositions of bulk precipitation while passing through the canopy. Two general questions were addressed: (1) What are the variations in rainfall, throughfall, stemflow and epikarst spring constituent fluxes in this forest? (2) How do the constituent fluxes in rainfall, throughfall and stemflow affect karst dynamic system and karst ecosystem?

Research area

This study was conducted at the Nongla karst dynamic system monitoring site, a village in the center of Guangxi Autonomous Region, China, situated at 108°19′E, 23°29′N (Fig. 1). This site is located in the subtropical monsoon climate zone. The annual mean temperature is 19.8. The annual precipitation is about 1,700 mm. The landform is peak-cluster karst, which has many steep peaks and two deep closed depressions. The outcrop of rocks is mainly dolomite of the Donggangling Group of Devonia. But the dolomite is some argillaceous and silicaeous component part. In 1950s, like other karst regions South China, forest vegetation in Nongla was destroyed, resulting in rock desertification. Since 1963, the local people had closed off hillsides to facilitate afforestation. Until today, the secondary forest has been forming a secondary arboreous forest, which is dominated by evergreen broad-leaved forest, such as *Cyclobalanopsis glauca*, *Cinnamomum saxitilis*, *Cinnamomum burmanni* BL, Folium Clicis Latifoliae. The extent of canopy cover of the secondary forest is 95% (Cao et al. 2005).

Field sampling and laboratory methods

From April to August 2006, field sampling was carried out in the Landiantang Epikarst Spring's water conservation forest region and its area is less than 1 km^2 (Zhang et al. 2004). Effective precipitation was collected using three plastic rain guages (surface area = 200 cm^2) which were installed in the adjacent four-storey building. The rain guages were covered with nets in order to prevent insects and other miscellanies from entering them. Incident throughfall was collected with 6 polyethylene funnels of 26 cm diameter (Roberto et al. 2001). The collectors were randomly installed in the forestry. Stemflow was collected using polyurethane collars attached to the selected trees in an upward spiral pattern and ending in closed 596-ml polyurethane bottles attached to the trees as described by Likens and Eaton (1970). For practical reasons, only trees with diameter breast height (DBH at 1.3 m) $\geq$10 cm were selected for stemflow measurements. Stemflow was measured for selected trees per size class of 10 cm. In the case of tall forest, the selected trees were 15, which distributed in the diameter classes 10 to <20, 20 to <30, 30 to <40 and > 40 cm. In the medium forest, the selected trees were 15, which distributed in the diameter classes 10 to <20, 20 to <30 and 30 to <40 cm. In the low forest, the selected trees were 15, which were in the size class 10–20 cm DBH. The same kind of water samples coming from different collectors and trees were mixed and then two 125-ml bottles of rainfall, throughfall and stemflow for chemical analysis were collected. After each incident rainfall, two 125-ml bottles of Landiantang Epikarst Spring water were collected at once.

All the collectors and funnels were carefully cleaned with dilute nitric acid and rinsed four to six times with deionized water before each collection. Sub-samples for chemical analysis were put in clean 125-ml polyethylene bottles. Each 125-ml sub-sample was brought to the field laboratory and stored at 4°C. One of the two 125-ml bottles of each kind of sub samples was placed and transported in a cooler for a general analysis (HCO_3^-, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, K^+,

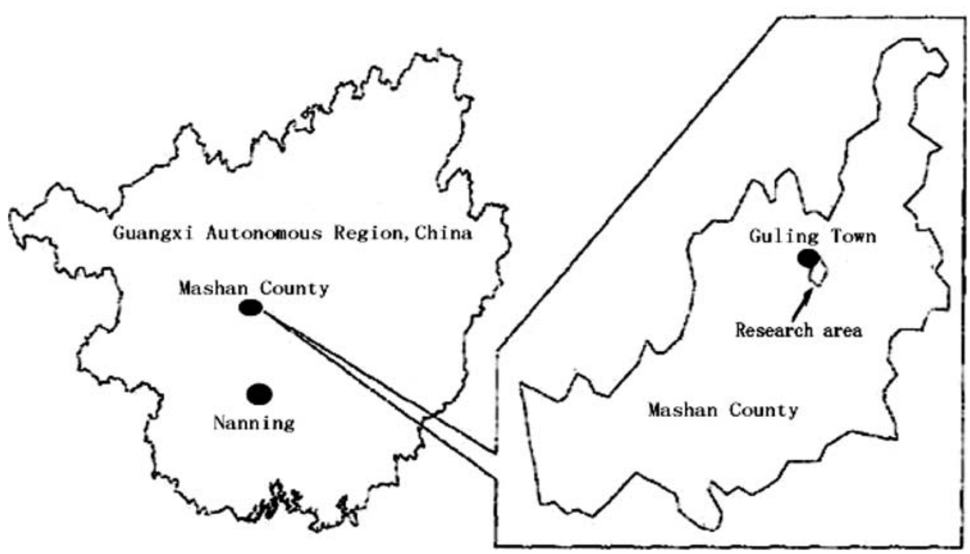

Fig. 1 Location of research area

free CO_2) to the laboratory of Institute of Karst Geology, CAGS, Guilin, China. The other was applied to measure total organic carbon including suspension and solution in all water samples (Luo et al. 2004). Total carbon (TC), total inorganic carbon (TIC) and total organic carbon (TOC) were measured using TOC-VCPN (DaoJin, Japan). Conductivity and pH of each samples were determined in the field by using Multiline P3 (WTW , Germany). pH was recalibrated every day.

Data manipulation

Some statistics were made by using Excel software (Version 2003) and correlation was analyzed by using SPSS software (Version 13.0). Sketches were drawn with Origin software (Version 7.0). In this paper the data on the water samples were the mean because the chemical characteristics of rainfall were limited largely by the factor of the environment. Net leaching was defined as the cation concentration of throughfall,stemflow and spring minus that in rainfall, the coefficient of leaching as the cation of throughfall,stemflow and spring over that in rainfall and the coefficient of variation as the mean over standard variance.

Results and analysis

The constituent fluxes of rainfall-throughfall and stemflow-spring reflected the balance of water chemistry and the features of matter's cycle (Tian et al. 2002). Nelda et al., have reported that the mean concentrations of nutrients in throughfall and stemflow were significantly higher than those in incident rainfall (Nelda and Noemi 2006). Similarly, the total chemical contents in throughfall, stemflow and spring were increased in contrast with those in rainfall as reflected in this paper. The concentration of chemicals of rainfall was in the order $HCO_3^- > Cl^- >$ free $CO_2 > Ca^{2+} > Mg^{2+} > Na^+ > K^+ > SO_4^{2-}$; While the concentration of chemicals in throughfall was in the order $HCO_3^- > Cl^- >$ free $CO_2 > Ca^{2+} > K^+ > Mg^{2+} > Na^+ > SO_4^{2}$; In stemflow $HCO_3^- >$ free $CO_2 > Cl^- > Ca^{2+} > K^+ > Mg^{2+} > Na^+ > SO_4^{2}$; In spring $HCO_3^- > Ca^{2+} > Mg^{2+} > SO_4^{2-} > Cl^- >$ free $CO_2 > K^+$. HCO_3^- , which is the first in all orders may be one of the characteristics of the precipitation in karst. Cl^-, Ca^{2+} and free CO_2 followed behind HCO_3^- in rainfall, throughfall and stemflow. In spring, Mg^{2+}, Ca^{2+} and SO_4^{2-} followed behind HCO_3^-. The different orders of chemical elements' concentration in rainfall, throughfall and stemflow reflected that chemical compositions had been changed differently by the secondary forest. Coefficients of variation of spring were the smallest in all water samples. It was shown that Landiantang spring's chemical characteristics were stable. It reflected the epikarst zone in Landiantang having the large function of regulation and this may be attributed to the forest vegetation on it (Jiang and Yuan 1999) (Table 1).

The trend of lower Cl^- concentrations in throughfall and stemflow suggested a remarkable absorbing when rainfall

Table 1 Chemical content of different waters in Nongla mg L−1 (April–August 2006)

	Compartments	Cl^-	SO_4^{2-}	HCO_3^-	K^+	Na^+	Ca^{2+}	Mg^{2+}	Free CO_2
Rainfall ($n = 11$)	Average	6.8	0	10.16	0.15	0.52	3.36	0.61	3.81
	Standard deviation	2.99	–	4.44	0.18	0.72	2.14	0.53	1.74
	Variation coefficient	0.44	–	0.44	1.22	1.38	0.64	0.88	0.46
	Maximum	14.03	–	16.9	0.5	1.98	7.32	1.73	6.8
	Minimum	3.51	–	4.23	0	0	0.81	0	1.7
Throughfall ($n = 11$)	Average	6.48	0	8.76	0.75	0.19	2.81	0.7	4.55
	Standard deviation	2.97	–	3.93	0.9	0.3	1.25	0.61	2.02
	Variation coefficient	0.46	–	0.95	1.2	1.61	0.45	0.88	0.44
	Maximum	14.03	–	17.33	2.56	0.93	4.88	1.73	8.5
	Minimum	3.51	–	4.23	0	0	1.22	0	1.7
Stemflow ($n = 11$)	Average	5.53	0	15.43	2.66	0.08	3.84	1.19	6.1
	Standard deviation	1.82	–	6.38	1.48	0.14	1.17	0.58	2.61
	Variation coefficient	0.33	–	0.41	0.56	1.68	0.3	0.49	0.43
	Maximum	8.18	–	25.35	6.23	0.44	6.1	2.47	11.89
	Minimum	3.51	–	5.78	1.45	0	2.44	0.49	2.61
Spring water ($n = 11$)	Average	6.8	8.59	371.48	0	0.64	75.89	30.99	5.72
	Standard deviation	1.26	4.01	26.9	–	0.09	6.97	4.76	1.15
	Variation coefficient	0.18	0.47	0.07	–	0.13	0.09	0.15	0.2
	Maximum	8.18	13.64	401.38	–	0.75	90.22	37.47	6.8
	Minimum	4.68	4.68	325.36	–	0.46	69.09	4.76	1.15

went through the forest vegetation (Yawney and Leaf 1970). No SO_4^{2-} existed in bulk precipitation, it indicated that there was no SO_4^{2}–S contamination. The higher concentrations of HCO_3^- and free CO_2 when rainfall went through the forest vegetation may be attributed to the respiration of the forest. Free CO_2 coming from the respiration of the secondary forest in throughfall and stemflow could alter the intensity and way of karstification and accelerate carbon rocks' dissolving (Yuan 1997). Higher concentration of Cl^-, HCO_3^-, SO_4^{2-}, Na^+, Ca^{2+} and Mg^{2+} in spring was attributed to the karstification (Table 1).

K^+ was increased remarkably in contrast with the other positive cations and was 11 times more in stemflow as in rainfall. Zhou et al. (2003), have reported that K^+ mainly leached from leaves in throughfall. Jiang (1997) has reported that there was K^+ in Landiantang spring. However, K^+ was not found in spring in this study. It was suggested that K^+ was absorbed by soil and diluted by bulk precipitation. Na^+ was decreased in throughfall and stemflow in contrast with in rainfall. Moreover, the concentration of Na^+ was the lowest in all cations in throughfall and stemflow, indicating that Na^+ content in air was low (Zhou et al. 2003). The concentration of Na^+ was increased rapidly after bulk precipitation passed through the soil layer and epikarst zone. So, we speculated that leaching, washing in soil layer and epikarst zone's karstification, play an important role in the increasing of Na^+ in spring. The range of variation of Ca^{2+} and Mg^{2+} was small because Ca^{2+} and Mg^{2+} move difficultly and are uneasy to be leached (Zhou et al. 2003). Positive karstification resulted in the large increasing of Ca^{2+} and Mg^{2+} in spring (Table 1).

According to the leaching coefficient, throughfall was enriched in the order $K^+ > Mg^{2+} > Cl^- > HCO_3^- > Ca^{2+} > Na^+$. Cl^-, HCO_3^-, Na^+ and Ca^{2+} in throughfall were leached negatively. K^+ and Mg^{2+} were leached positively. The stemflow was enriched in the order $K^+ > Mg^{2+} > HCO_3^- > Ca^{2+} > Cl^- > Na^+$. Cl^- and Na^+ were leached negatively while all the others were leached positively. The concentrations of K^+, Mg^{2+}, HCO_3^- and Ca^{2+} in stemflow were higher than in throughfall. It was attributed that they were leached from the stems and leaves. It was significant for the nutrient element's redistribution in soil because the stemflow was mainly put into the soil along the roots. Spring was enriched in the order $HCO_3^- > Ca^{2+} > Mg^{2+} > Na^+ > Cl^- > K^+$. It was the stereoscopic, spatial, multi-layer output of rainfall after redistribution in karst ecosystem and it was also a kind of output of nutrient elements in underground runoff (Tian et al. 2002). Jiang Zhongcheng has reported that the moving order of Ca^{2+}, Mg^{2+}, Na^+ and K^+ was $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ between lithosphere and hydrosphere. This study agreed with it. The moving coefficient between rainfall and spring was in the order $Mg^{2+} > Ca^{2+} > Na^+ > K^+$. It was different from Jiang's (1997) findings on the moving order of nutient elements between lithosphere and hydrosphere. It might be attributed to absorbing and leaching of the secondary forest, soil, and dilution of bulk precipitation (Table 2).

Rainfall was acidified by the secondary forest in non-karst region, such as Young Second-rotation Chinese Fir Plantations in Huitong, China (Tian et al. 2002) and Chinese Fir Plantation in Nanping, China (Pan et al. 1996). In the secondary forest, pH of throughfall and stemflow, such as maximum, minimum and mean, were lower than rainfall's, indicating that the karst forest vegetation could also acidify rainfall to some degree. In karst regions, when precipitation with lower pH flows into soil layer and epikarst zone, which is characterized by abundant calcium and prejudiced alkalinity geochemical background, it can buffer alkalinity, activate some alkali elements and improve their effective states. All these favor the vegetation to absorb adequate nutrient element, accelerate vegetation's succession, decrease karst ecosystem's fragility. From maximum to minimum, the variation of pH in spring was small, which means that the spring restored steady chemical characteristics (Fig. 2).

The relationship between total acidity and free CO_2 was linear. The correlation of total acidity with free CO_2 was significant at the 0.01 level (two-tailed). Pearson correlation coefficient was 0.899. It was suggested that the increasing of free CO_2 brought about the increasing of total acidity's, and it was significant for karstification (Yuan 1997) (Fig. 3).

Total carbon, organic carbon and inorganic carbon in throughfall and stemflow were increased in contrast with

Table 2 Net leaching amount and leaching coefficient of throughfall, stemflow and spring (April–August 2006)

Compartments	Cl^-	HCO_3^-	K^+	Na^+	Ca^{2+}	Mg^{2+}
Net leaching of throughfall (mg L^{-1})	−0.32	−1.39	0.6	−0.33	−0.55	0.09
Net leaching of stemflow (mg L^{-1})	−1.27	5.27	2.51	−0.44	0.48	0.58
Net moving of spring (mg L^{-1})	0	361.33	-0.15	0.12	72.52	30.39
Leaching coefficient of throughfall	0.95	0.86	4.95	0.36	0.84	1.15
Leaching coefficient of stemflow	0.81	1.52	17.53	0.16	1.14	1.96
Moving coefficient of spring	1	36.58	–	1.24	22.57	51.19

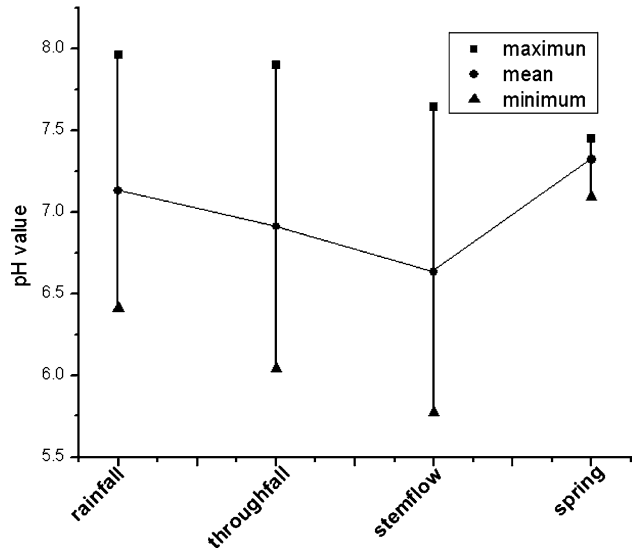

Fig. 2 Variation of different water pH value

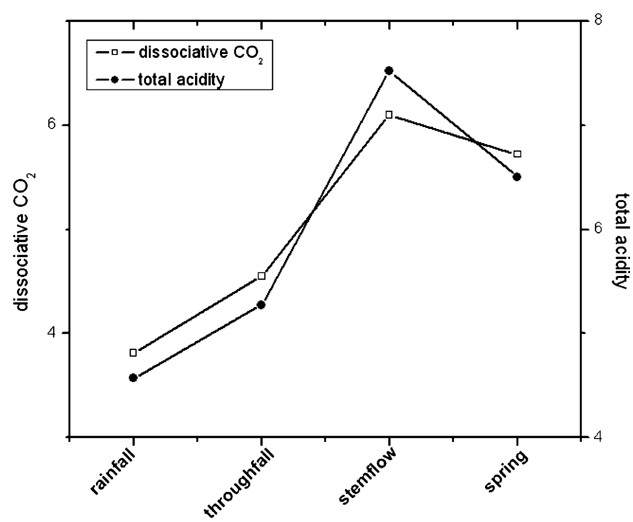

Fig. 3 The relationship of dissociative CO_2 and total acidity in different water

open land rainfall. Some organic compositions coming from the leaves and stems were leached into the bulk precipitation, and it led to the increasing of organic carbon (Luo et al 2004). We speculate that the increase of dissolved CO_2 results in the increase of total inorganic carbon. From rainfall to throughfall and stemflow, the total inorganic carbon was increased mainly due to free CO_2, which was dissolved more in throughfall and stemflow. In spring, the total inorganic carbon was increased mainly due to the strong karstification when bulk precipitation flew through the epikarst zone (Jiang and Yuan 1999). The variation of total carbon was the same as the variation of total inorganic carbon. It was mainly affected by total inorganic carbon while little affected by total organic carbon (Fig. 4).

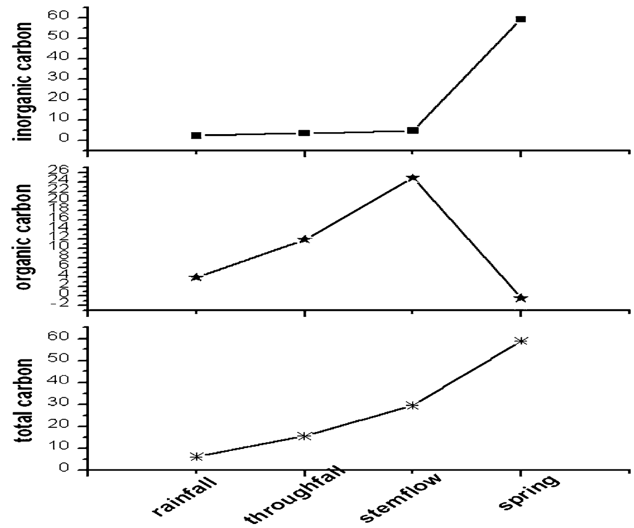

Fig. 4 TC, TOC and TIC content in different water

Conclusions and discussions

The chemical characteristics of precipitation via the secondary forest were changed: some of the chemicals were increased. Some were decreased. Different elements showed different variations. Cl^- and Na^+ were decreased. Cl^- was decreased from 6.8 mg L^{-1} in rainfall to 5.3 mg L^{-1} in stemflow, similarly, Na^+ was decreased from 0.52 mg L^{-1} in rainfall to 0.08 mg L^{-1} in stemflow. K^+, Mg^{2+}, HCO_3^-, Ca^{2+} and free CO_2 were increased. K^+ was increased from 0.15 mg L^{-1} in rainfall to 2.66 mg L^{-1} in stemflow; Ca^{2+} from 3.36 mg L^{-1} in rainfall to 3.84 mg L^{-1} in stemflow; Mg^{2+} from 0.61 mg L^{-1} in rainfall to 1.19 mg L^{-1} in stemflow; HCO_3^- from 10.16 mg L^{-1} in rainfall to 15.43 mg L^{-1} in stemflow; Free CO_2 from 3.81 mg L^{-1} in rainfall to 6.1 mg L^{-1} in stemflow. The increasing chemical input into the karst ecosystem were good for the vegetation. Total carbon, total inorganic carbon and total organic carbon were alsoincreased. Total carbon was increased from 6.04 ppm in rainfall to 29.5 ppm in stemflow; Total inorganic carbon was increased from 2.11 ppm in rainfall to 4.65 ppm in stemflow; Total organic carbon was increased from 3.92 ppm in rainfall to 24.86 ppm in stemflow. Carbons' increase made the precipitation erode more strongly. pH of throughfall and stemflow was descended, which was 7.13 in rainfall, 6.91 in throughfall and 6.63 in stemflow. Comparing to the rainfall, chemical components in spring varied indistinctively and the range of pH in spring was small. In the process of experiment, the variation coefficient of spring was smaller than that of rainfall. For example, the variation coefficient of Cl^- was 0.44 in rainfall, but 0.18 in spring; the variation coefficient of HCO_3^- was 0.44 in rainfall, but 0.07 in spring; the variation coefficient of Na^+ was 1.38 in rainfall, but 0.13 in spring; the variation coefficient of Ca^{2+} was 0.64 in rainfall, but 0.09 in spring; the variation coefficient of Mg^{2+} was 0.88 in rainfall, but 0.15 in spring; the variation coefficient of Free CO_2 was 0.46 in rainfall, but 0.2 in spring. The variation range of pH was from 6.41 to 7.96 in rainfall, but was from 7.09 to 7.45 in spring. All these reflected the large regulating function of the forest vegetation on the epikarst zone.

Precipitation via the secondary forest can lead to further karstification, accelerate the biogeochemical cycle in epikarst zone, enhance some alkali elements' effective states in soil, supply vegetation with more nutrients, advance vegetation's growth and succession. It is reasonably sufficient to form a stable karst ecosystem.

The species of water conservation forest in Landiantang spring's water conservation area are complex and diverse. Different species change the quantity and quality of precipitation differently (Yu et al. 2003). This paper only reflected roughly the trend of chemical characteristics of precipitation via forest vegetation. However, it cannot reflect the influence of specific species on precipitation. It is necessary to compare the influence of different species on precipitation and provide suitable species for restoration and rehabilitation in karst areas.

In karst areas, some rocks are uncovered and forests grow directly on uncovered rocks. Some rocks are covered with soil layer. The variations of precipitation's chemical characteristics via the uncovered rock are different from those via the rocks covered with soil layer. It is necessary to take variations of chemical characteristics of precipitation via soil layer into consideration.

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