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Short Communication

Hydrochemical Response of Epikarst Spring to Rainfall: Implications of Nutrition Element Loss and Groundwater Pollution

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Abstract

High-resolution measurements of rainfall, water level, pH, conductivity, temperature, [K^+], [NO_3^-] and [Ca^{2+}] of the Landiantang epikarst spring at Nongla, Mashan County in Guangxi Province, China were recorded by using data loggers with a time interval of fifteen minutes. The results showed that the pH of the Landiantang Spring dropped and the conductivity fell as well. As Ca^{2+}, Mg^{2+} and HCO_3^- were the dominant ions, the linear relationships between conductivity and those ions were developed to calculate variations in SI_C, SI_D and $LogP_{CO2}$ of the spring during rainfalls. The $LogP_{CO2}$ of Landiantang Spring during rainfalls was lower than that at lower flows, and its SI_C and SI_D also were lower. It can be figured out that the dilution of precipitation controls the hydrochemical variations of Landiantang Spring during rainfall, and the water-rock-gas interactions control the hydrochemical variations of the spring at the usual time. The process of water-rock-gas is universal to Landiantang Spring because after rainfall, gas with high CO_2 concentration dissolves in water flowing as spring, which in turn becomes more highly undersaturated, dissolves more dolomite to make up for the effect of precipitation dilution, and the conductivity renews slowly after rainfall. However, to explain the hydrological and chemical changes, the dilution of precipitation may be more important during rainfall, because it is the key process to controlling the chemical evolutions of the spring. The [K^+] and [NO_3^-] rise rapidly as the [Ca^{2+}] falls during rainfall. Therefore, an important conclusion is hypothesized that the restricted growth of plants in karst regions is possibly caused not only by the low labile trace elements in soil, but also by the loss of these nutritional elements in the ecosystem. Moreover, fertilizers, for example, can also be brought away through the epikarst zone by flowing water due to high fissure and permeability of the epikarst zone, which will contaminate epikarst spring and groundwater, and may produce serious environmental problems. Thus, how to develop effective solutions to karst water-related environmental challenges will become the primary study of karst aquifers and water resources in the future.

Keywords: epikarst zone, hydrochemical data logging, loss of nutritional elements, hydrochemical variation, groundwater pollution, storm effect

Introduction

In southwestern China, the karst area spreads widely and the karst ecosystem is fragile [1, 2]. In recent years, a growing concern with water and soil erosion and groundwater pollution in the epikarst zone has been mentioned [3, 4]. Therefore, "Global Study of Karst Aquifers and Water Resources" of IGCP 513 was approved by the IGCP and UNESCO to encourage international cooperation to increase understanding of karst water resources

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Table 1. Total and labile contents of trace elements in soil in Nongla, Guangxi.

SP	element	B	P	K	SiO_2	Ca	Mg	Mn	Cu	Zn	Fe	Na
A	whole	106.50	723	6,367	343,900	32,631	19,227	2,006.50	23.15	431.60	131,300	2018
	labile content	0.32	2.36	39.65	684.50	2,568.50	990.60	23.62	0.45	0.50	13.98	10.40
	efficiency (%)	0.30	0.33	0.62	0.20	7.87	5.15	1.18	1.94	0.12	0.01	0.52
AB	whole	87	602	5524	343,200	25,237	17,844	1780	18.91	411	130,000	1,048
	labile content	0.16	1.62	28.50	925.90	2,039.90	838.50	17.51	0.23	0.19	15.21	9.38
	efficiency (%)	0.18	0.27	0.52	0.27	8.08	4.70	0.98	1.22	0.05	0.01	0.90
B	whole	76.30	571	5,986	338,900	23,268	16,773	1367	23.13	414.80	132,500	1,437
	labile content	0.15	2.29	29.27	384.50	1,650.60	741.43	12.89	0.32	0.21	14.39	9.65
	efficiency (%)	0.20	0.40	0.49	0.11	7.09	4.42	0.94	1.38	0.05	0.01	0.67
CS	whole	115.30	1264	11,959	379,900	29,829	20,191	2755	40.52	413.1	121,400	1,112
	labile content	0.11	6.47	32.25	432.80	4,209.60	95.65	31.62	0.85	1.11	9.35	10.40
	efficiency (%)	0.10	0.51	0.27	0.11	14.11	4.87	1.15	2.10	0.27	0.08	0.94

Total and liable content of soil elements is measured in mg/kg; SP stands for soil profiles; CS stands for cranny soil.

with regard to both ecological and human health concerns, and to promote the sharing of ideas, experiences and resources in developing solutions to karst water-resource challenges.

In the past, although hydrochemical processes have been evaluated in karst systems in a wide variety of settings, and significant progress has been made in understanding conditions in the extensive subtropical tower, karst areas of southwestern China, there has been little high-resolution study of hydrochemical processes in karst systems touched upon to reveal aquifer structure and behavior [5-8]. There has barely been consideration of changes in concentrations of ions (such as K^+, NO_3^- and Ca^{2+}) in epikarst springs after rainfalls. Thus by analyzing the geological background of southwestern China, the Landiantang epikarst spring has been selected for monitoring (2003-05) and study of the hydrochemical variations and nutrition element loss during rainfall within an area of well-developed peak cluster karst (*Fengchong* in Chinese) at Nongla, Mashan County in Guangxi Province, China. The purpose of this ongoing work is to investigate a karst hydrogeological system in the peak cluster region. This paper focuses on the storm effect and the information it provides about water-related environmental problems.

However, an understanding of detailed hydrochemical variations of the epikarst system, especially during rainfall, is very difficult to catch due to the rapidity of the flow and chemical variations that characterize the storm effect in well-developed flow systems in the karst regions. Magnitudes and rates of changes, which are very crucial to understanding the response of karst system during rainfall, the key processes controlling the ions variation and chemical evolution of the system, are recorded only after the high-resolution, multiparameter data logging methods are developed. As a result, the continuous hydrochemical monitoring equipment was utilized to understand the hydrochemical variations and investigate the problems of groundwater pollution and nutrition element loss in the epikarst area, which will provide new knowledge for water and soil erosion and groundwater pollution.

Geological Backgrounds

Nongla (108º19'E, 23º29'N) in Guangxi Province, China is famous for its typical epikarst development and rapid ecological restoration 20 years after deforestation. Many papers on ecological restoration, biodiversity and element migration have been published [9]. However, few researchers have touched upon the hydrochemical variations of epikarst spring and nutrition element losses during flood periods [10].

Local rock is made of argillaceous and siliceous dolomite of the Donggangling Formation of Devonian. Therefore, Ca and Mg are relatively abundant in the stone and soil, and the content of trace elements such as Al, Fe, Zn, Si, P, B and K in the rock is high (Table 1) [11]. The annual mean temperature of Nongla is about 20ºC and annual rainfall is 1,756.6 mm. The thickness of soil is about 0.5 m, and the soil CO_2 content changes from $4,500\times10^{-6}$ to $28,000\times10^{-6}$, depending on the seasons. After 20 years of ecological reconstruction, biodiversity increased remarkably, the habitat was improved and the community developed into a more stable stage. The local vegetation is mainly composed of natural forest and plantation. By investigating the biodiversity and the ecology, the species abundance is similar to that in the tropic forest at Liulian hill in Hainan Province, China [12]. According to good eco-environmental conditions, a perennial karst spring develops in the epikarst zone (Fig. 1).

Table 2. Hydrochemistry of Landiantang Spring.

data	Auto logging data		In-situ data			Laboratory values							WATSPEC results		
	Temp	pH	Cond	Ca^{2+}	HCO_3^-	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	SI_C	SI_D	$LogP_{CO2}$
	ºC		μs/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L			
6/24[a]	20.0	7.38	624	82.80	427.80	0.21	0.44	79.13	44.63	1.44	3.26	425.05	0.31	0.62	-3.06
8/7[a]	20.8	7.32	598	80.30	420.90	0.50	0.50	78.22	36.08	1.48	9.04	406.96	0.27	0.45	-2.61
10/12[a]	20.4	7.49	624	80.00	434.70	0.07	0.65	87.83	43.06	1.53	11.30	425.05	0.49	0.91	-2.48
1/3(M)[b]	14.3	7.80	565	73.00	448.50	0.06	0.33	69.79	40.29	1.27	2.79	379.83	0.58	1.08	-3.14
1/3(A)[b]	14.5	7.68	563	70.00	441.60	0.07	0.35	71.90	39.02	1.25	3.36	382.61	0.48	0.86	-3.05
1/3(E)[b]	14.9	7.70	559	72.00	434.70	0.06	0.28	68.95	40.04	1.28	2.18	384.01	0.49	0.91	-3.25
5/1[b]	19.3	7.48	464	66.00	345.00	0.02	0.28	70.92	24.62	5.06	6.14	313.90	0.27	0.32	-2.04
1/25[c]	15.5	7.59	471	/	/	0.14	0.68	58.05	30.75	5.12	12.74	320.87	0.25	0.41	-2.16
2/25[c]	13.3	7.83	488	/	/	0.12	0.61	70.00	31.24	4.10	3.92	297.95	0.50	0.81	-2.44
3/30[c]	16.9	7.63	414	/	/	0	0.34	53.15	23.80	6.50	9.80	262.55	0.20	0.26	-2.27
5/6[c]	19.1	7.53	448	/	/	0	0.37	66.00	26.39	5.57	3.81	323.30	0.30	0.44	-2.07
5/1[b] rain	27.5	7.54	35.9	/	/	0.22	0	0.74	0.34	0.89	1.00	4.44	-3.18	-6.40	-3.86
3/30[c] rain	18.3	7.57	39.8	/	/	0.12	0.19	1.44	2.34	3.48	1.00	9.92	-2.67	-4.91	-3.59

[a] hydrochemical data in 2003;
[b] hydrochemical data in 2004;
[c] hydrochemical data in 2005;
M stands for morning, A for afternoon, and E for evening;
/ stands for lack of data.

Methods

The methods include hydrochemical data logging, in-situ titrating and sample analysis in the laboratory.

A U-20 mulitilchannel data logger (made by Horbia in Japan) automatically records temperature, pH, specific conductivity, $[K^+]$, $[NO_3^-]$ and $[Ca^{2+}]$ of the epikarst spring in-situ, with resolution of 0.1ºC, 0.01 pH, 0.01 μs/cm, 0.1 mg/L, 0.1 mg/L and 1 mg/L. A CTDP300 mulitilchannel data logger (made by Greenspan in Australia) automatically recorded rainfall, water level, temperature, pH, specific conductivity of the spring in-situ, with resolution of 0.1 mm, 0.01 cm, 0.1ºC, 0.01 pH and 0.01 μs/cm with a time interval of fifteen minutes. The data of temperature, pH and specific conductivity recorded by the two mulitilchannel data loggers are very similar. In order to keep the consistency of hydrochemical data, only the data of rainfall recorded by a CTDP300 is used to make up for the shortage of the U-20 mulitilchannel data logger. Although the U-20 mulitilchannel data logger is convenient for monitoring the ion concentration, it is not easy to calibrate due to the instability and calibration taking a long time. By hydrochemical data logging, the hydrochemical response of the epikarst spring to storm events can be precisely revealed.

In-situ titrating is used to measure the $[HCO_3^-]$ and $[Ca^{2+}]$ of water with the Aquamerck Alkalinity test and Hardness test (made in Germany). The resolutions are 6 mg/L and 1 mg/L, respectively.

To understand the distributions of other major ions in the system, water samples were collected and taken to the laboratory for monthly analysis. Unstable parameters (temperature, pH and specific conductivity) were measured in-situ. Bicarbonate was analyzed by standard titration; K^+ and Na^+ were analyzed through atomic absorption spectrophotometry; Mg^{2+} and Ca^{2+} were titrated by ethylene diamine acid (EDTA); Mohr titration was used for analyzing Cl^- and SO_4^{2-}. Those data have in turn allowed the calculation of key parameters describing carbonate chemistry, including the saturation index with respect to calcite (SI_C), the dolomite saturation index (SI_D) and CO_2 partial pressure ($LogP_{CO2}$) assumed to be in equilibrium with sample waters.

In order to obtain values of SI_C (saturation index of calcite), SI_D (saturation index of dolomite) and $LogP_{CO2}$ (CO_2 partial pressure), WATSPEC software was used [13]. Equilibrium is attained if SI_C or $SI_D>0$, spring water is supersaturated with respect to calcite or dolomite; if SI_C or $SI_D<0$, spring water is aggressive to calcite or dolomite; and if SI_C or $SI_D=0$.

Moreover, in order to obtain the soil CO_2, the soft tube was embedded into the soil with 20 cm deep. when the CO_2 partial pressure in the soft tube was steady-going, soil CO_2 was measured by Gastec (made in Japan) monthly or yearly.

Results

Calculation of SI_C, SI_D and $LogP_{CO2}$

Table 2 shows the hydrochemical properties of the Landiantang Spring between 2003 and 2005. It can be seen that the concentrations of HCO_3^-, Ca^{2+} and Mg^{2+} dominate among the significant ions present. The water is thus an HCO_3-Ca-Mg type, which reflects the control of the Donggangling dolomite on water chemistry at the site.

To get continuous values of SI_C, SI_D and $LogP_{CO2}$, the concentration of HCO_3^-, Ca^{2+} and Mg^{2+} (Laboratory values) is calculated first by equation [14]:

$$[HCO_3^-] = Cond \cdot 0.72056-24.56007,\ r^2=0.97 \quad (1)$$
$$[Ca^{2+}] = Cond \cdot 0.10955+12.41526,\ r^2=0.85 \quad (2)$$
$$[Mg^{2+}] = Cond \cdot 0.09589-16.167,\ r^2=0.95 \quad (3)$$

Where the concentrations of ions are mg/L and Cond stands for specific conductivity and is corrected for 25ºC (Fig. 2).

Because of the low concentrations of K^+, Na^+, Cl^- and SO_4^{2-} (Table 2), which are used in WATSPEC to calculate SI_C, SI_D and $LogP_{CO2}$, their variations with time are neglected when calculating SI_C, SI_D and $LogP_{CO2}$ by using the average values in Table 2 for the four ions [15].

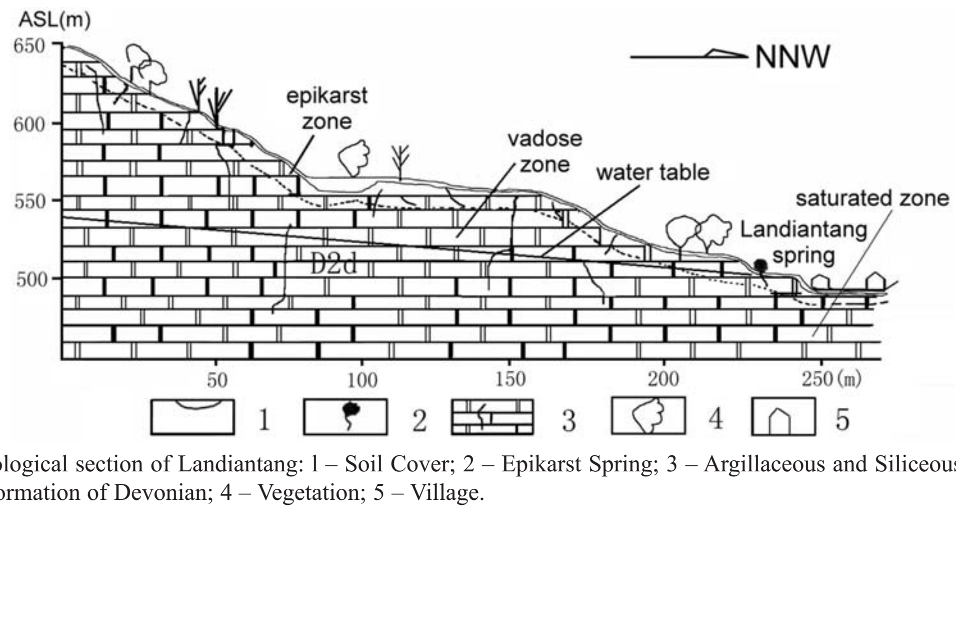

Fig. 1. Hydrogeological section of Landiantang: 1 – Soil Cover; 2 – Epikarst Spring; 3 – Argillaceous and Siliceous Dolomite of the Donggangling Formation of Devonian; 4 – Vegetation; 5 – Village.

Storm Hydrochemical Response of the Landiantang Spring

From Fig. 3 it can be seen that the pH, specific conductivity, [Ca^{2+}], SI_C, SI_D and $LogP_{CO2}$ of the Landiantang Spring all fell, while water level, water temperature, [K^+] and [NO_3^-] increased during rainfalls. On August 5, 2003, there was 34.5 mm rainfall in 2.5 hours. Although the magnitudes of the water-level fluctuations are small (about 0.02 m), the temperature of the spring increased quickly from 20ºC to 20.9ºC, pH dropped from 7.24 to 7.15, specific conductivity fell by 135 µs/cm, $LogP_{CO2}$ dropped from -1.65 to -1.72, SI_C decreased from 0.17 to -0.06, and SI_D decreased from 0.33 to -0.22 during the rainfall in a short time. These results illustrate that dilution of rainfall is a key process controlling hydrochemical variations of Landiantang Spring during rainfall. Rainfall with high temperature in summer season, and low pH, specific conductivity, SI_C, SI_D and $LogP_{CO2}$ (Table 2), travels through the karst system with a high percentage of fissure and permeability rapidly to dilute the spring, which affects the hydrochemical variations of the spring and makes the spring aggressive to dolomite. Moreover, the dilution of rainfall also can be proven according to Fig. 2. When it is raining, the rainfall with low conductivity will decrease the concentrations of Ca^{2+}, Mg^{2+}, and HCO_3^- in the spring. The variations of Ca^{2+} in Landiantang Spring on August 5 reflects the storm effect, 21.7 mg/L in 2.5 hours, indicating the predicated direction of precipitation dilution.

Although rainfall magnitudes are small (about 10 mm on August 7), the hydrochemical variations are similar to those on August 5, which also reflects the storm hydrochemical response of Landiantang Spring.

It is difficult to summarizing the findings of the results of this monitoring work without reference to the full dataset as presented in Fig. 4. The time series comprises two levels of detail. Firstly, time series for the full data record are presented in Fig. 4 for Landiantang Spring, showing the seasonal variability superimposed on the fine detail of diurnal and storm-scale fluctuations. Secondly, a more detailed time series showing diurnal fluctuations for the springs are presented in Figs. 3 and 4 for a three-day time series from August 5 through August 7, 2003. Though we lack the full data of [K^+], [NO_3^-] and [Ca^{2+}] to analyze their overall behaviors to the rainfalls all year due to the instability and calibration-taking time of U-20, the two figures still provide a graphical representation of similar hydrochemistry variations under different rainfall intensity. This is because rainfall is a key process controlling hydrochemical variations of the Landiantang Spring.

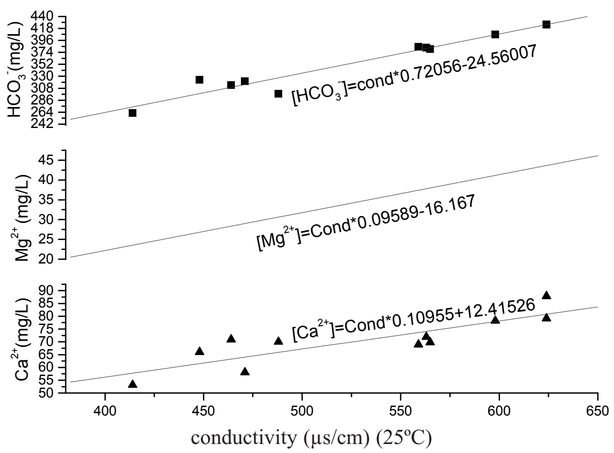

Fig. 2. Relationship between [Ca^{2+}], [Mg^{2+}], [HCO_3^-] and conductivity in Landiantang Spring.

Element Migration and Groundwater Pollution in Epikarst System

Any plant for metabolism must absorb N, P and K from soil, and 70% N in the soil exists as nitrate. Without enough nutrition, plants will be runtish.

By analyzing the labile content of trace elements (e.g. Al, Fe, Zn, Si, P, K, B) of Nongla soil (Table 1), though the labile trace elements in Nongla soil are quite high, the efficiency of these elements is relatively low, which will restrict plant growth [11]. Therefore, in poor soil, especially in karst area, mass fertilizer will be used for enhancing harvest.

As we all know, the epikarst is at the active part of the rock cycle, atmospheric cycle, biological cycle and water cycle, where the carbon-water-calcium cycle activizes intensively and dissolution of carbonate rocks is quick. This makes the high percentage of fissure and permeability in the epikarst zone. Therefore, water-soluble elements like K^+ and NO_3^- can leach more easily [16]. It can be seen from Fig. 3 that this is the case, i.e. while it is raining, K^+ and NO_3^- as plant nutrition elements are lost in water, showing the increase in concentrations of these ions in the spring.

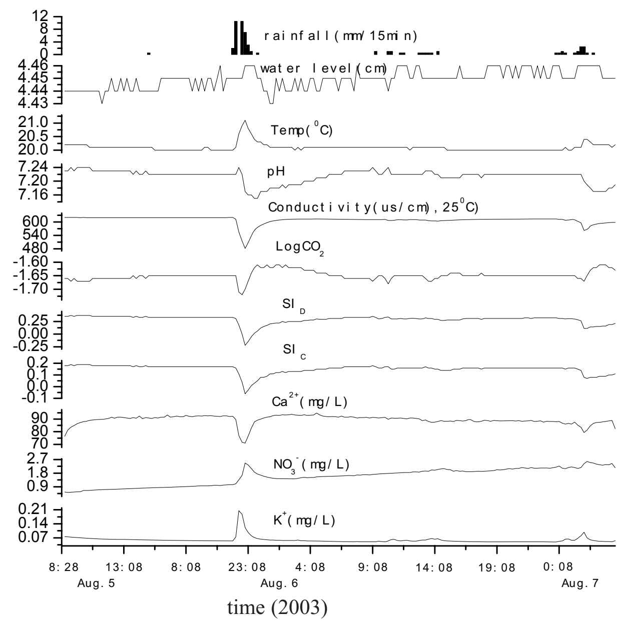

Fig. 3. Hydrochemical variations after rainfalls on August 5-7, 2003.

On August 5, the concentrations of K^+ and NO_3^- increased by 1.5 mg/L and 1.7 mg/L, respectively, in a short time. On August 7, the magnitudes of the rainfall are very small, so the change of K^+ and NO_3^- is still similar. However, the variation of $[NO_3^-]$ is different from $[K^+]$ and keeps slowly increasing after rainfall for a long time, which will contaminate the water resource in the karst regions. On the other hand, it is inferred that the formation of rocky desertification and the restricted growth of plants are caused not only by the low labile content of trace elements in the soil, but also possibly by the loss of trace nutrition elements in the epikarst zone (Figs. 3 and 4).

Soil CO_2 for Karst Processes

Yuan Daoxian [17] brought forward the theory that the karst dynamic system is composed of $CaCO_3$(solid) – CO_2(gas) – H_2O(liquid) and soil CO_2 is very crucial in driving karst processes [18, 19]. When soil CO_2 enters water it will enhance the dissolution of carbonate rocks, which in turn increases the concentrations of HCO_3^- and Ca^{2+} in water [20].

From Fig. 5, it shows that soil CO_2 partial pressure (P_{CO2}) near Landiantang Spring changed remarkably from 1993 to 2004. Related to this, the $[Ca^{2+}]$, $[Mg^{2+}]$ and $[HCO_3^-]$ in Landiantang Spring also will show the remarkably coincidental change, because carbonate rock weathering is very sensitive to soil CO_2 change.

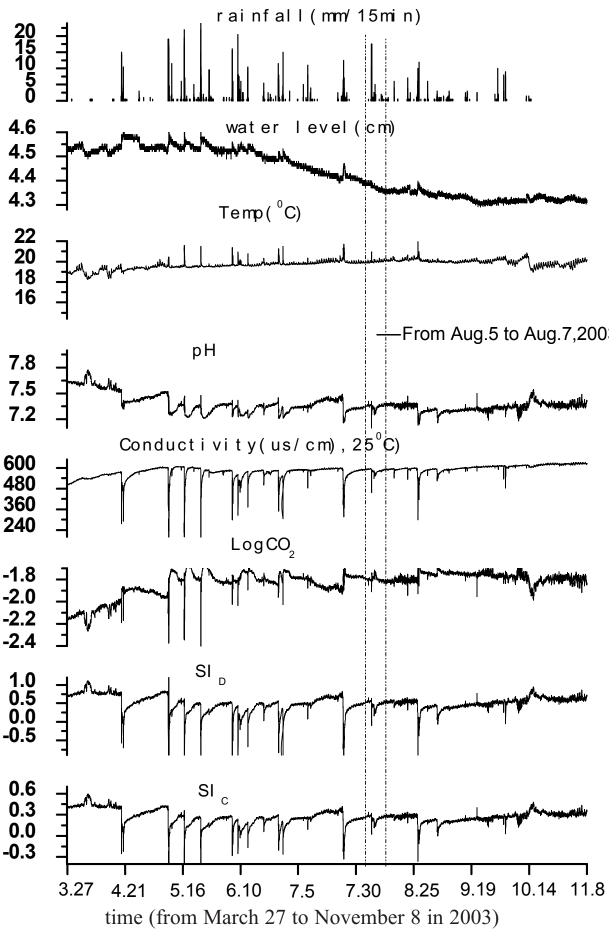

Fig. 4. Hydrochemical variations of Landiantang Spring from March 27 to November 8 in 2003.

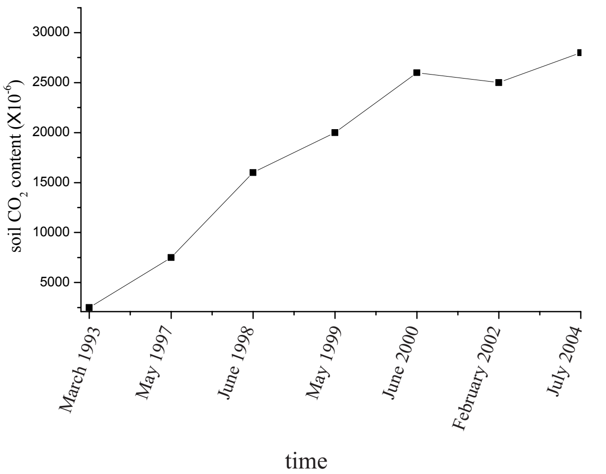

Fig. 5. The annual change of soil CO_2 content in 20 cm depth.

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \Leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$$

In addition to reforestation and ecological restoration, it is estimated that soil CO_2 partial pressure will increase slowly and will enhance the karst processes and soil formation in the Nongla epikarst zone. Moreover, the change of soil CO_2 partial pressure by controlling the process of water-rock-gas affects the hydrochemical evolution of Landiantang Spring at an usual time and it is crucial in mitigating the dilution of rainfall on the spring hydrochemistry after rainfall. On the other hand, carbonate rock weathering contributes to the CO_2 atmospheric sink (the process will decrease the release of soil CO_2 into the atmosphere, and thus contributes to the CO_2 atmospheric sink).

Discussion

The hydrochemical variations of Landiantang Spring during two different magnitudes of rainfalls were similar, which can interpret the hydrochemical behavior during flood plus and water-related environmental problems in the karst region. Moreover, it can be seen that a mulitilchannel data logger is a powerful tool for understanding hydrological and chemical changes of karst spring within minutes of all times.

Considering the chemical variations and nutrition loss occurring short time-scales during rainfall in this system, it is concluded that the hydrological and chemical changes of Landiantang Spring during rainfall were mainly controlled by the dilution of precipitation. However, the water-rock-gas interactions should not be neglected because pH, a major controlling variable within the $CaMg(CO_3)_2 - CO_2 - H_2O$ system, rises in response to rising concentrations of dissolved dolomite after rainfall, which eases up the dilution of rainfall. In addition, the water-rock-gas interactions also are very crucial in controlling the hydrochemical evolutions of the spring without rainfall.

While it is raining, the pH of the spring rapidly falls as conductivity drops in the study site in short time-scales with the addition of rain, which suggests that rainfall dominated the change of the spring. The highly buffered rainfall with lower CO_2 partial pressure moves quickly through the system to significantly influence the Landiantang Spring because the flowing rainfall has no time to dissolve soil CO_2, which in turn can increase the concentration of Ca^{2+}, Mg^{2+} and HCO_3^-. The decrease in $[Ca^{2+}]$ affirmed the facts that the spring did not dissolve soil CO_2 to make it aggressive to dolomite. Moreover, the decrease in SI_C and SI_D, among the most fundamental parameters in direction reflect the dilution of precipitation with the decrease of CO_2 partial pressure. In addition, when rainfall moves quickly through the soil and the epikarstic zone, it will dissolve some water-soluble elements that can produce the problem of nutrition loss. If some pollutants are transmitted by rainfall, the water resources in the karst regions will be contaminated and the contamination is hazardous to humans.

In contrast to the behavior of the spring during rainfall, the water-rock-gas interactions control the hydrological and chemical changes after rainfall. After rainfall, the soil CO_2 slowly enters the water, which in turn makes the spring undersaturated and dissolves more dolomite to make up for the decrease of Ca^{2+}, Mg^{2+} and HCO_3^-. Moreover, the rainfall can stay in the soil for a long time and slowly flows as spring in the studying site for its good eco-environmental condition. Therefore, the water-rock-gas interactions are the key processes in controlling the hydrochemistry and determining the value of pH without raining. In addition, to the ecological restoration, the soil CO_2 partial pressure will increase slowly and enhance the reaction:

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \Leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3$$

...which will make the pH drop accordingly and accelerate the karst processes and soil formation at Nongla.

Conclusions and Future Work

By hydrochemical data logging of Landiantang Spring and monitoring soil CO_2 content over many years, the hydrochemical character and its environmental effects on epikarst spring were well known. Furthermore, the driving action of soil CO_2 also was clearly explained.

Firstly, the hydrochemical variations of the Landiantang Spring during rainfall was mainly controlled by the dilution of precipitation and the water-rock-gas interactions control the hydrochemical variations of the spring at the usual time.

Secondly, the low labile content of trace elements in the karst area and nutrition loss both lead to the restricted growth of plants and enhance rocky desertification.

Thirdly, agricultural pollutants and nutrition loss mainly happened during rainfall and were brought into groundwater, and spring during rainfall via the epikarst zone produces new pollution. Therefore, how to prevent agricultural pollutants getting into water will become the focus in karst areas in the future.

Though the hydrological and chemical changes of Landiantang Spring have been achieved, the continuous and long process to measure hydrochemical behavior at Nongla is not enough and the analyzing results of water samples are comparatively few. In addition, due to the instability and calibration time of U-20, some basic questions are still unanswered concerning water-related environmental problems and the differences of hydrochemical variations in the karst regions of southwest China. We hope a new mulitilchannel data logger will be invented to clarify the aqueous geochemistry of karst aquifer and water-related environmental problems in karst regions.

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References

1. YUAN D., LI B., LIU Z. Karst in China. Episodes. **18**, (1), 62, **1995**.
2. YUAN D. On the Karst Ecosystem. Acta Geologica Sinica. **75**, (3), 336, **2001**.
3. ALEX S., PATRICK P. E., CLAUDIO, KURT D., TAMMY P., GLENN A., ZHONG L. Groundwater quality. Water Environ Res. **69**, (4), 777, **1997**.
4. LANG Y., LIU C., ZHAO Z., LI S., HAN G. Geochemistry of surface and ground water in Guiyang, China: Water/rock interaction and pollution in a karst hydrological system. Applied Geochemistry. **21**, (6), 887, **2006**.
5. BROOK G. A., FORD D. C. The origin of labyrinth and tower karst and the conditions necessary for their development. Nature. **275**, (5680), 493, **1978**.
6. FIKRET K. Review of Groundwater Pollution and Protection in Karst Areas. Water Air Soil Pollut. **113**, (1-4), 337, **1999**.
7. LIU Z., CHRIS G., YUAN D., JOE M. South China aquifer storm-scale hydrochemistry. Ground Water. **42**, (4), 491, **2004**.
8. LIU Z., CHRIS G., YUAN D., JOE M., JIANG G., HE S., LI Q. Hydrochemical variations during flood pulses in the southwest China peak cluster karst: Impacts of $CaCO_3$-H_2O-CO_2 interactions. Hydrological Process. **18**, (13), 2423, **2004**.

9. LI Q., YU L., DENG Y., LI W., LI M., CAO J. Leaf epidermal characters of *Lonicera japonica* and *Lonicera confuse* and their ecology adaptation. J. Fores. Res. **18**, (2), 103, **2007**.
10. ZHANG C., YUAN D., CAO J. Analysis of the environmental sensitivities of a typical dynamic epikarst system at the Nongla monitoring site, Guangxi, China. Environ. Geol. **47**, 615, **2005**.
11. JIANG Z. Element migration in karst geochemical process of the dolomite in Nongla, Guangxi. Carsologica Sinica. **16**, (4), 304, **1997** [In Chinese with English abstract].
12. CHEN F., WU T. Guangdong plants. Science Publisher House: Beijing, pp. 15-50, **1982** [In Chinese].
13. WIGLEY T. M. L. WATSPEC: a computer program for determining equilibrium speciation of aqueous solutions. Br Geomorphol Res Group Tech Bull. **20**, 48, **1977**.
14. LIU Z., DREYBRODT W. Kinetics and rate-limiting mechanisms of dolomite dissolution at various CO_2 partial pressures. Science in China (B). **44**, (5), 500, **2001**.
15. STUMM W., MORGAN J. J. Aquatic Chemistry, 2nd edition.; Johan Wiley and Sons: New York, **1981**.
16. DWIVEDI U. N., MISHRA S., SINGH P., TRIPATHI R. D. Nitrate Pollution and its Remediation. In: Shree N. S. and Rudra R. T. (Ed.) Environmental Bioremediation Technologies. Springer Berlin Heidelber: German, pp. 353-389, **2007**.
17. YUAN D. Karst of China. Geological publisher house: Beijing, pp. 20-70, **1991**.
18. YUAN D. Contribution of IGCP 379 “karst process and carbon cycle” to global change. Episodes. **21**, (3), 198, **1998**.
19. YUAN D. IGCP 448: World correlation of karst ecosystem (2000-2004). Episodes. **23**, (4), 285, **2000**.
20. LIU Z., ZHAO J. Contribution of carbonate rock weathering to the atmospheric CO_2 sink. Environ. Geol. **39**, (9), 1053, **2000**.