Hydrochemistry Variations and Carbon Sinks of Cave Stream during a Storm Event

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Key words: Rainfall, cave stream, hydrochemistry, carbon sinks

Abstract: It is a key period to study the hydrochemistry of a cave stream during the storm events. In order to study the hydrochemistry variations and carbon sinks, the continuous monitoring of a stream in Xueyu cave was conducted during June 13-15. The hydrochemistry type of the stream was in a type of HCO_3-Ca. The geochemistry parameters, such as pH, conductivity, and water temperature, reacted to rainfall quickly. The response time of hydrochemistry to the rainfall was about 4 hours. Even affected by the piston effect, the variations for conductivity, HCO_3^- and Ca^{2+} were in negligible magnitudes during a prophase rainfall. The parameters of conductivity, HCO_3^- and Ca^{2+} declined after the rainfall as a result of the dilution effect, and the variation of calcite saturation index was consistent with Ca^{2+}. The water temperature rose from 16.50 ℃ to 16.58 ℃ due to the calefacient effect of the rainwater. Accompanied with the rise of the water temperature, the air temperature rose by 0.5℃. The carbon sinks of the studied cave stream were remarkable during the storm even, and the variations of partial pressure for CO_2 showed a notable increase after the rainfall. The stock of DIC in the cave stream increased by 15191 kg, and the absorbed CO_2 was 5479 kg during the storm event. Therefore, the role of cave stream in the carbon sinks should be paid more attentions.

1 INTRODUCTION

The karst area in Southwest China is about 53 km^2, it is the largest karst region in the world (Pu et al., 2010). As crannies and conduits well develop in this area, the cave streams are important for water supply in local area (Yuan, 2000). Due to the duality of water storage in surface ground and underground, the transform of surface and underground water is very quickly, especially during a storm event (Yang et al., 2012). With the obviously global climate change, the carbon sink caused by karst processes has been paid more attentions (Yuan, 2011). As we all know, the carbon sink could be driven by the formation of carbonate rocks in a long-time scale in the geologic history (Cao et al., 2011). The karst processes can happen in the normal atmospheric temperature with an open system, which is sensitive to the environment changing (Li et al., 2004; Zhang et al., 2005; Liu et al., 2005; Liu and Yuan, 2000). Therefore, it is important to study the karst process in a short-time scale, especially during a storm event (Liu and Zhao, 2000). Rainfall period is an important period to study the karst process, as we can monitor the response of the karst processes to the environment change (Liu et al., 2007). In this paper, a three days' monitoring of a cave stream was carried out during a storm event, and the objects of the study are: 1) to study the variations of hydrochemistry of the cave stream, and 2) to evaluate the carbon sinks of the cave stream during the storm event.

2 STUDY AREA

Xueyu cave (29°47′ N, 107°47′ E) is located in Fengdu county, Chongqing, China. It is on the bank of Long River, a branch of Yangtze River. It is about 16 km far away from the downtown of Fengdu. The altitude of the Xueyu cave entrance is about 233 m, which is about 55 m above water level of the Long River. The cave is developed in the Fangdoushan anticline, which is located in the paralleled ridge-valley area of east Sichuan. The cave follows the strike of the stratum, and the length of the cave is 1643 m. There are three floors in the cave, and the underground river is developed in the lowest floor,

Wang, X.
Hydrochemistry Variations and Carbon Sinks of Cave Stream during a Storm Event.
In *Proceedings of the International Workshop on Environment and Geoscience (IWEG 2018)*, pages 288-293
ISBN: 978-989-758-342-1

of which the water discharges to the Long river (Zhu et al., 2004). The temperature of the cave is in the ranges of 16-18 ℃, and temperature variations exist among different floors. The humidity is above 95% all the year round, and it is 100%in the floor with the stream flowing (Wang, 2010). With the subtropical monsoon climate, the mean annual precipitation of the study area is 1072 mm. Affected by the Southwest and Southeast monsoon, most of the rainfall is in April to September. The thickness of the overlying rock is 150 to 250 m, and the thickness of overlying soil is 0 to 90 cm. The local vegetation is evergreen broad-leaved forest and shrub (Pu et al., 2009).

3 METHODS

The data of water temperature, water stage, pH and conductivity from 13 June to 15 June, 2011 was collected from a Greenspan CTDP 300 multi-channel data logger, which was placed in the underground stream near the cave entrance. Water stage, water temperature, pH and electrical conductivity (Ec) were monitored every 15 minutes. The discharge was calculated by the model of Rectangular Weir at the cave entrance. The cave air temperature was obtained by the OM-EL-USB-2 multi-recorder, which is placed at the second floor of the cave, with the measurement range of -35~80 ℃ and accuracy of 1℃. In order to get the weather information, a Davis BS28-VP2 mini weather station was placed on a roof, which is about 500 m to the cave entrance. The wind speed, wind direction, air temperature, relative humidity, air pressure, and rainfall were recorded by the mini weather station. The samples of the rain water were collected during the study from 13 to 15 June, and the stream water samples were collected every month in 2011. All the water samples were collected by cleaned polythene bottles and acidified with 1:1 nitric acid. Cations of the water samples were measured in the geochemistry and isotopic laboratory of Southwest University by Perkin-Elmer Optima 2100DV ICP-OES, with accuracy of 0.001mg/L. Anions of the water samples were measured by Ion Chromatograph, with the accuracy of 1 ppb. The concentration of HCO_3^- was determined by the Aquamerck Alkalinity Test, with the accuracy of 0.1 mmol/L. The saturation index of calcite (SIc) and partial pressure of CO_2 (P_{CO_2}) were calculated by WATSPEC software.

4 RESULTS AND DISCUSSION

4.1 Hydrochemistry Variations of the Cave Stream

To study the hydrochemistry variations of the stream, the water samples were monitored every month in 2011. The equivalents per hundred of Ca^{2+} was 90.55%, it was 66.01% of HCO_3^- and 17.26% of Cl^-.. Data of the cations congregated on the side of Ca^{2+}, and the anions assembled on the side of HCO_3^- (Figure 1). Therefore, the hydrochemistry type of the stream water was HCO_3-Ca. The ratio of $(Ca^{2+}+Mg^{2+})/HCO_3^-$ was 0.48, which was close to 0.5 (Xiao et al., 2012). So, the weathering type of the drainage area for the cave stream was dominated by carbonate rock weathering.

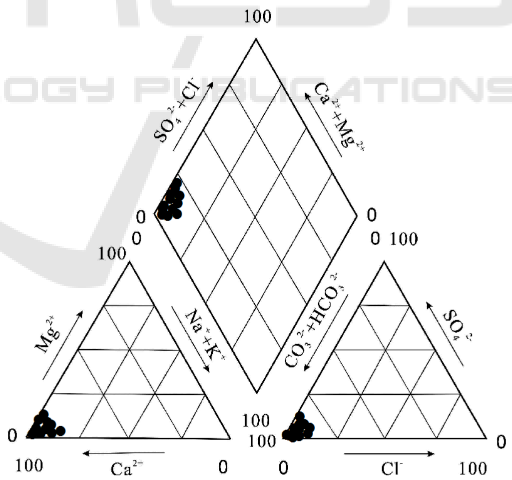

Figure 1: Hydrochemistry type of the underground water in Xueyu cave.

Table 1: Hydrochemistry of rain water and stream water (13~15 June, 2011)

Water type	T_w/℃	pH	EC/ (μS·cm^{-1})	Ca^{2+}/ (mg·L^{-1})	Mg^{2+}/ (mg·L^{-1})	Na^+/ (mg·L^{-1})	K^+/ (mg·L^{-1})	HCO_3^-/ (mg·L^{-1})	Cl^-/ (mg·L^{-1})	SO_4^{2-}/ (mg·L^{-1})	Sr^+/ (mg·L^{-1})	Si^+/ (mg·L^{-1})	NO_3^-/ (mg·L^{-1})
Rain	24.2	5.76	92	6.315	0.151	0.111	0.188	6.1	7.373	4.846	0.015	0.123	2.159
Stream	16.5	7.62	405	102.213	2.395	0.985	0.473	219.6	16.023	16.503	0.831	3.775	8.025

4.2 Rainfall'S Effects on the Hydrochemistry Variations of the Cave Stream during a Storm Event

4.2.1 Hydrochemistry of Rainwater

There were two rainfall periods during the study from 13-15June. The first period was from 11:30 to 14:30 June 13, and the precipitation was 11 mm. The second phase was from 22:30, 13 June to 5:30, 14 June, and the precipitation was 69.6 mm. The total precipitation was 80.6 during the study (Figure 2). The temperature was about 25℃ before the first rainfall, but it dropped to 22℃ during the first rainfall event. The pH of the rain water was 5.76, which was closed to 5.6, the pH of acid rain. The acid rain in Chongqing area was featured by high concentrations of Cl^-, NO_3^-, and SO_4^2 (Chen et al., 2012)-. As Cl^- is steady in the hydrological cycle and is little affected by human activities (Meybeck, 1979) Therefore, Cl^- was an important parameter to evaluate the rainfall's effects on the variations of surface water hydrochemistry (Grosbois et al., 2000). The ratio of Na^+/Cl^- in sea water was 0.86 (Meybeck, 1979), but the ratio for rain water during 13-15 June was 0.015, which indicated the rain water was merely affected by sea water. The temperature of rain water was higher than that of the cave stream water (Table 1), therefore, the stream water could be heated by the rain water. The concentrations of Ca^{2+} and Mg^{2+} in rain water were lower compared with those of the stream water, so the hydrochemistry of the stream water would be lightly affected by the rainfall.

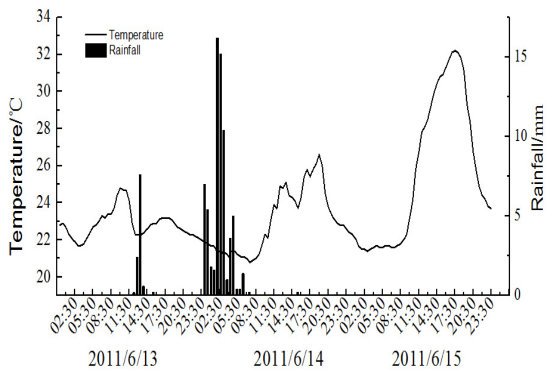

Figure 2: The variations of rainfall precipitation and air temperature from June 13 to June 15, 2011.

4.2.2 The Hydrochemistry Variations of the Cave Stream Water

The data of water temperature, pH and Ec could get from the CDTP 300 multi-channel data logger during the rainfall period. The coefficient R^2 between Ca^{2+} and EC was 0.732, and it was 0.856 between HCO_3^- and EC. Therefore, the concentrations of Ca^{2+} and HCO_3^- could be calculated by the Formula 1 & 2.

$$[Ca^{2+}]=0.209\cdot Ec+5.454 \quad (1)$$

$$[HCO_3^-]=0.751\cdot Ec - 62.75 \quad (2)$$

The first rainfall didn't cause the hydrochemistry variations of the stream water due to the little precipitation (Figure 3). The water in the soil was saturated after the first rainfall, and the coming rainfall in the morning of 13 June could become overland flow, which would flow into the stream quickly. Affected by the rainfall, the discharge of the stream reached the peak at 3:00, 13 June. The time lag between the rainfall and the highest discharge was about 4 hours. The pH of the stream water was 7.93 before the second rainfall, but it dropped to 7.65 after the rain water pouring into the stream. The reasons for the pH dropping were: the dissolved CO_2 in the stream water, and mixture of the stream water and the rain water with low pH. The concentrations of HCO_3^-, Ca^{2+} and Ec in the stream water showed no obvious variations before the second rainfall. However, the concentrations of HCO_3^-, Ca^{2+} and Ec rose markedly during the second rainfall, which was attributed to the old water in the soil and cranny was pushed out by rain water. Dilution effect dominated the variations of the hydrochemistry of the stream water after the rainfall, and the concentrations of HCO_3^-, Ca^{2+} and Ec decreased. When the rainfall came to maximum, the saturation index of calcite in the stream water was above zero, which indicated the calcite in the water was saturated and the erosion ability of the stream water was weak. The variations of the saturation index of calcite was consistent with HCO_3^-, Ca^{2+} and Ec, which was mainly affected by old water in the soil and cranny.

4.2.3 Rainfall's Effects on the Temperature of the Cave Air and the Stream Water

In summer, the temperature of the atmosphere is higher than that of the cave stream water (Yang et al., 2009). The rain water will be heated by atmosphere, soil and vegetation when flowing on the ground surface. The first rainfall was not adequate to form surficial runoff, and the stream water was little affected by the first rainfall. The temperature of the atmosphere decreased in the night of June 13 (Figure 3), which could influence the water's temperature (Figure 4). With the precipitation of the rainfall becoming larger in the morning on June 14, the heated rain water poured into the cave stream, and the temperature of the stream water rose slowly, reaching a peak value of 16.58 ℃ at 2 o'clock, June 14 (Figure 4). As a result of lacking heat to make the temperature of the stream water get higher, the temperature of the stream water became lower (Figure 4). After the air's temperature became higher in the afternoon on June 14, the stream water's temperature increased slowly.

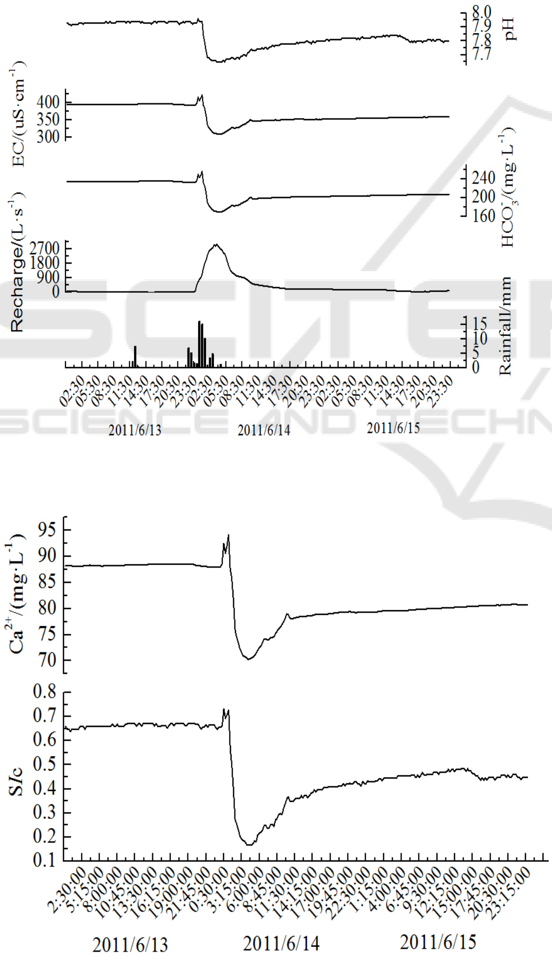

Figure 3: Variations of pH, EC, HCO3-, Ca2+, discharge, and SIc of stream water from June 13 to June 15, 2011.

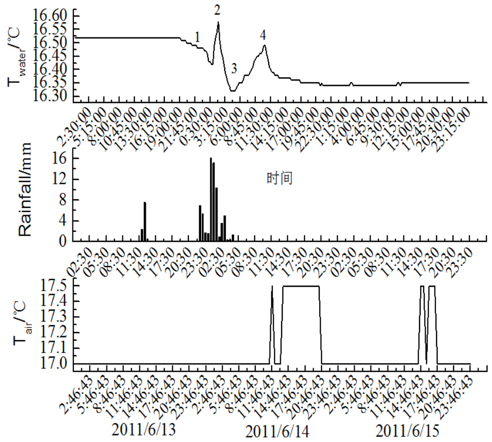

Figure 4: Variations of water temperature and air temperature in Xueyu cave from June 13 to June 15, 2011.

Previous studies showed that the variations of cave air's temperature related to the climate change, altitude, ventilation, rainfall event (Stoeva et al., 2006). Besides, cave air's temperature can vary in periods of 24 hours and 12 hours due to the variations of the atmosphere's temperature (Sondag et al., 2003). With three floors and only one entrance in Xueyu cave, the ventilation of the cave was indistinctively. There was no fluctuation in the temperature of the cave air during no rain period (Figure 4), which indicated the temperature of the cave air was stable in day and night. However, the stream water's temperature increased after the second rainfall (Figure 4). The cave air's temperature rose to 17.5 °C 10 hours after the rainfall, and the cave air's temperature dropped to 17.0 °C at 20:00 on June 14, and rose to 17.5 °C again at 14:00 on June 15. It was about 10 hours from the rise of stream water's temperature to the rise of cave air's temperature. Therefore, the rainfall affected the variations of the cave air's temperature, which followed the rise of the stream water's temperature.

4.3 Carbon Sinks in the Stream Water during Rainfall Event

Dissolved inorganic carbon (DIC) in stream water comes from Karst process by absorbing CO_2 and the weathering of carbonate rock (Jiang, 2000). Some studies found that dissolved CO_2 in the water was more stable than we thought (Adamczk et al., 2009), which made the carbon sinks can be evaluated during the rainfall periods. HCO_3^- is the main form of DIC in the water when pH is below 8.2 (Cao, 2012). The pH of the stream water during the rainfall

period from June 13 to June 15 was below 8.0, therefore, the amount of DIC was equal to the amount of HCO_3^- in the stream water.
Fllowing the reaction equation of the karst processes:

Limestone:

$$CaCO_3+CO_2+H_2O — Ca^{2+}+2HCO_3^- \quad (3)$$

Dolomite:

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

The absorbed CO_2 in the underground water can be calculated:

The amount of absorbed CO_2 (mg/s) = $1/2[HCO_3^-]\times 44\times Q$ (Liu, 2000) (5)

($[HCO_3^-]$ is the concentration of HCO_3^-; Q is the discharge of the underground water.)

The amount of DIC (mg/s) = concentration of DIC $\times Q$ (6)

The concentration of DIC increased firstly and then declined to the minimum value when the rainfall reached the maximum (Figure 5). With old water pouring into the stream, the concentration of DIC increased in the prophase of the rainfall. However, the concentration of DIC decreased, which was affected by the dilution effect of the rainfall. Though the concentration of DIC decreased, the amount of DIC in the stream increased due to the increase of the discharge, rising from 15.0 g/s to 511 g/s. The amount of absorbed CO_2 increased with the increase of discharge, from 5.94 mg/s to 184 mg/s. The variations of the partial pressure of CO_2 indicated that the partial pressure of CO_2 increased with more CO_2 dissolved in the stream water.

The total amount of dissolved CO_2 during the rainfall period was 6202 kg, and total amount of DIC was 17198 kg. The amount of dissolved CO_2 increased by 5479 kg, and the amount of DIC increased by 15191 kg compared with those of pre-rainfall period. The reason for the increase of dissolved CO_2 and DIC were that the increase of the discharge of the stream and the erosion of carbonate rocks.

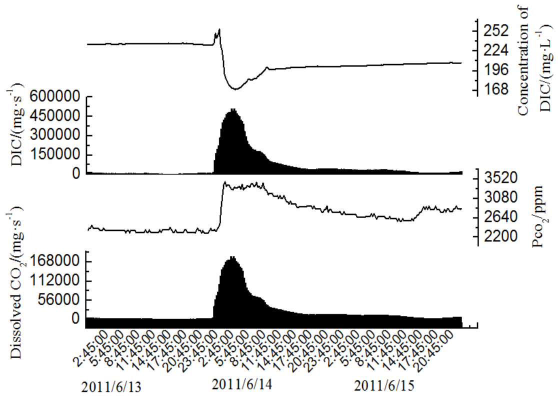

Figure 5: Variations of Pco2, absorbed CO2 and DIC of stream water from June 13 to June 15, 2011.

5 CONCLUSIONS

The hydrochemistry type of the cave stream water is HCO_3-Ca, and the weathering type in the study area carbonate weathering. The hydrochemistry of the stream is merely affected by the rainfall. Piston effect and dilution effect dominated the variations of the hydrochemistry of the stream.

The discharge of the stream increased after the rainfall during the study. The decrease of the pH during the rainfall was due to the CO_2 effect and the mixture of rain water. Affected by the piston effect, the concentrations of HCO_3^- and Ca^{2+}, and Ec all showed increase trends during the early rainfall period. However, the dilution effect dominated the decrease of HCO_3^- , Ca^{2+}, and EC after the rainfall became heavier, and the saturation index of calcite also showed a decrease trend. The temperature of the stream water increased during the rainfall period, and the response time of the stream was 4 hours. Cave air's temperature was also increased after the rainfall, and the response time was 10 to 28 hours.

The amount of DIC was 17198 kg transported by the stream water during the study, and the amount of dissolved CO_2 in the water was 6202 kg. The amount of dissolved CO_2 increased by 5479 kg, and the amount of DIC increased by 15191 kg compared with those of pre-rainfall period.

ACKNOWLEDGEMENT

This study was supported by the Start-up funds for doctoral research of China West Normal University (412654).

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