

THE HYDROCHEMICAL RESPONSE OF CAVE DRIP WATERS TO DIFFERENT RAIN PATTERNS (A CASE STUDY FROM VELIKA PASICA CAVE, CENTRAL SLOVENIA)

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Abstract: Data on temperature and water discharge from four permanent drips (VP1-VP4) were logged since June 2006 at one hour intervals within the Velika Pasica Cave, located in central Slovenia south of Ljubljana. In order to clarify the hydrochemical response of drip water to the water supplement regime, Drips VP1 and VP2 were selected for detailed analyses by monitoring the response of electrical conductivity (EC) and major ions to different rain events in 2011 and 2012. Two types of rainfall can be classified: “diffuse rainfall” and “concentrated rainfall”, and they affected the variation of electrical conductivity (EC) differently. It had two main characteristics at VP1: i) it had an obvious response to the dilution effect whenever the intensive rainfall occurred; ii) After the fast flow from concentrated rain events, it had a process of slow flow dissolution, with decreased EC; while during the diffuse rain events it could arrive at the dissolution equilibrium, rising to a stable EC. While due to the seepage flow at VP2, the piston effect dominated there. Meanwhile, the Mg/Ca ratio in the cave drip water showed a distinct pattern over time, influenced by the prior calcite precipitation (PCP) effect and the retention time, which was affected by different rain patterns. The precipitation regime is one of the principal impacts on drip water hydrochemistry, but other factors should be considered in future studies.

Key words: Cave drip water, rain regime, hydrochemistry, Mg/Ca

1. INTRODUCTION

Karst caves, as a form of direct access into the interior of karst aquifers, provide opportunities in order to understand details of both background hydrogeochemical processes and the movement of ground water within aquifers (Baker & Brunsdon, 2003; Fairchild et al., 2006). Until recently, much work has focused on waters in the vadose zone, and in particular on speleothem drip waters which can elucidate details of physical and chemical processes in the unsaturated zone (Baker et al., 2000; Tooth & Fairchild, 2003). In contrast, a more detailed understanding of the hydrological functioning of karstic systems is being developed by high-resolution, automated sampling. Studies of frequently -measured or automatically -logged discharges illustrate a clear presentation of

hydrological responses to infiltration events (Baker et al., 1997; Genty & Deflandre, 1998; Fairchild et al., 2006; McDonald & Drysdale, 2007).

Studies of high-resolution have focussed directly on the analysis of hydrochemical variation in drip water are increasing (Hu et al., 2008). Major dissolved ions, such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , etc. have been widely applied in studies on drip water mixing processes in the unsaturated zone above caves (Huang et al., 2001; Tooth & Fairchild, 2003; Fairchild et al., 2006). Frenández-Cortès et al., (2008) stated that the variation in drip water electrical conductivity is closely linked to residence time, after discussing the details of the piston effect in cave seepage water (Genty & Delandre, 1998; Baker & Brunsdon, 2003). Within recent years, as research techniques and knowledge have moved forward, some attention has been paid to the ratio of Mg/Ca in

cave drip waters, suggesting that its variation is related to contrasting wet and dry climatic conditions (Huang et al., 2001). Precipitation is one of the main driving forces in a cave's hydrodynamic system, which ultimately controls the drip water in the caves. The rate of cave drip water from a stalactite is highly dependent on the rainfall regime (Frenández-Cortès et al., 2008). The rainfall patterns as an important impacts on the drip water flow was discussed in detail from high resolution data collected by high-resolution equipment (Liu & Brancelj, 2011), however, still rare studies discussed the rain regimes acting as an impact on the cave drip water hydrochemistry in detail.

In order to reveal the process of karst water hydrochemical evolution in the vadose zone, and the hydrochemical response to rainfall over different seasons, a high-resolution, multi-parameter data logger has been used to monitor continuous hydrodynamic variations and a high-frequency hydrochemical sampling regime has been carried out in the Velika Pasica Cave (Slovenia).

In this article: first, we divided the rain patterns as “diffuse rainfall” and “concentrated rainfall”, according to the different amounts, intensity and frequency. The concentrated rainfall preformed as high intensity and short duration, while on the contrary, the diffuse rainfall falls lightly but has longer duration.

Second, we discuss the response of electrical conductivity in drip waters to five rain events from August (summer) to December (winter) in 2011 (for VP1) and one event in 2012 (for VP2), a period that reflects different rain patterns in response to the local seasonal climatic change.

Last, the response of the Mg/Ca ratio in the same period is also discussed.

These results from the cave is also related to the concurrent cave ecological system research (Brancelj, 2002), as there is a significant correlation between the hydrological and ecological research which will be further presented in the future.

2. CAVE SITE DESCRIPTION

The Velika Pasica Cave (GPS site of the cave entrance: 45°55'7.35"N, 14°29'35.17"E) is located 20 km south of Ljubljana, adjacent to the village of Gornji Ig with the cave entrance at the elevation of 662m a.s.l. (Figs. 1 & 2). The thin Norian-Retian dolomite bedrock outcrops in the cave area with the strata inclining to the north at 10-15° (Pleničar, 1970). Approximately three hundred metres to the southwest, at the elevation of 765 m a.s.l., a higher hill descends towards to the cave with approximately

15° slopes. There are some gradual slopes and several depressions (dolina) on the northeast side.

The cave is positioned almost on the top of the karstic plateau, with characteristics of a typical shallow cave, as the ceiling of the gallery has a maximum thickness of 10 -12 m, while at some points it may only be 2-5 m thick. On the surface above the cave, a thin layer of soil varies from 0 - 20 cm. There is no surface water within a radius of 3 - 4 km around the cave area, apart from a small spring (on average < 0.1 l/s) (Brancelj, 2002). The cave is a 126 m long horizontal gallery rich in decorations of flowstone (Fig. 2). A 10 m deep circular depression with a diameter of 15 m forms the entrance to the cave. This entrance is the only known outlet connecting with surface (Brancelj, 2002).

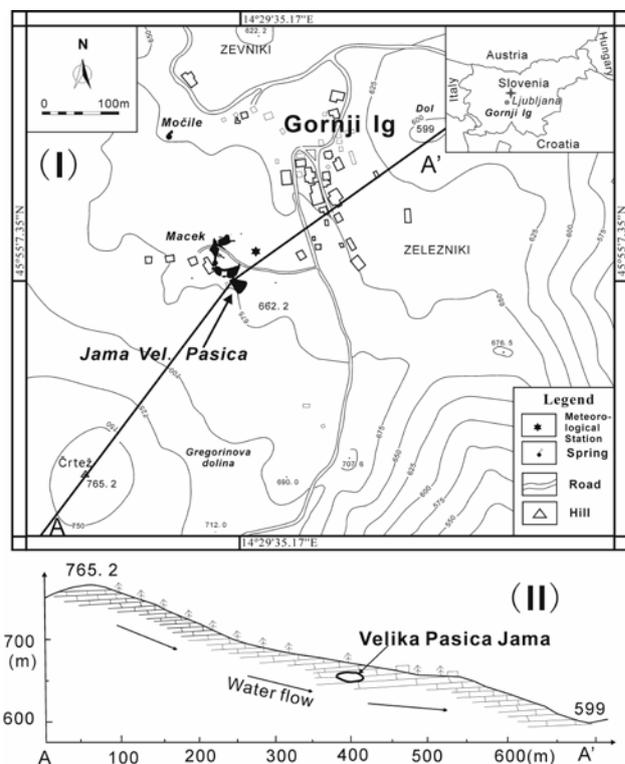


Figure 1. (I) Location of the Velika Pasica Cave (Slovenia).

The black figure: the Velika Pasica Cave. The main symbols in the map: *: the outside meteorological station; Δ: the highest point of the region - Črtež Hill; ●: the temporary spring - Močile Spring. (II) The geological profiles of the cave area (A-A').

All water within the cave is exclusively percolating water, entering the cave as permanent or temporary drips from the ceiling or temporary flows (after heavy rain or intensive snow-melt) from the side. Several sinkholes are distributed across the cave (Fig. 2), and some small standing water bodies are located nearby in muddy pools. The cave can be divided into two parts (Fig. 2): the outer part with two chambers and the inner part with two other chambers. Four

permanent drips, designated as VP1, VP2, VP3, and VP4, are distributed within the cave in each chamber. The outer part and the inner part are connected by a 0.7 meter high \times 1.0 meter wide passage.

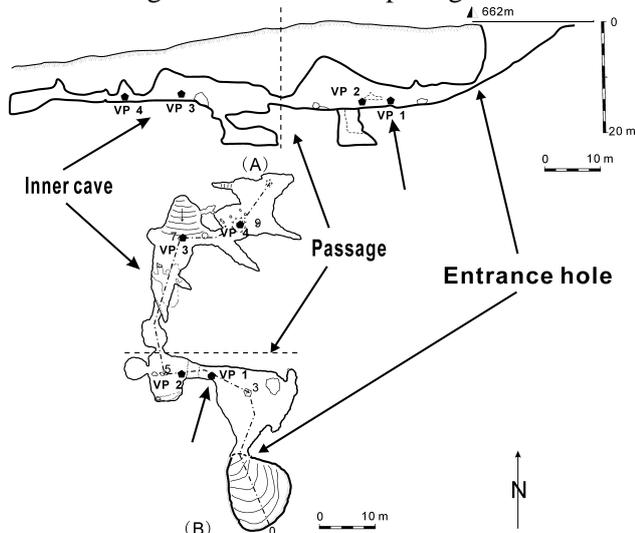


Figure 2. Cross-section (A) and ground plan (B) of the Velika Pasica Cave (Slovenia). VP1 – VP4: permanent dripping points. The arrowhead points the drip VP1 and the drip VP2 located adjacently which were analysed in detail in this article.

3. MATERIAL AND METHODS

Four permanent drippings were monitored in the cave by means of sensors connected to a data-logger (DL2e, Delta-T Device Company) since June, 2006. In order to measure discharge, under each drip there was placed a set of rain gauges with accuracy and resolution of ± 0.2 mm (measured by tip bucket). A plastic screen (2 m \times 2 m) was erected in order to collect dripping water and direct it into the funnel of the rain gauge. Discharge was integrated over one hour intervals and expressed as m^3/s when it was analyzed. Probes (resistivity type with a range of measurement of -25 to $+100^\circ\text{C}$ and a digital resolution of 0.1°C) for water temperature were inserted into the lower part of each rain gauge, while probes for air temperature were 50 cm distant and positioned 1m above the cave floor. Both temperatures were measured in 4-hour intervals.

An automatic water sampler was designed for drip water collection in a 60 ml PVC bottle each hour. Every 24h, the electrical conductivity (EC) and pH of the samples were measured by a Multi 340i instrument with accuracy $\pm 1\%$ and a MultiCal pH-540 meter with accuracy 0.01 on their arrival in the laboratory. Based on the variations in EC, some typical samples were chosen for chemical analysis by ion chromatography (Methrom 761 Compact IC), which included: K^+ , Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- and

NO_3^- ions. Samples selected for chemical analyses on major ions were refrigerated at 5°C and analysed within 48 hours after collection. Other specific calculations, e.g. CO_2 partial pressure ($p\text{CO}_2$) and Saturation Index of Calcite (SIc) were carried out with PHREEQC (Appelo & Postma, 2005).

A meteorological station, with sensors for air temperature and precipitation connected to another data-logger (DL2e, Delta-T Device Company) was established on the surface, adjacent to the cave entrance (Fig. 1). The sensor settings replicated those inside the cave.

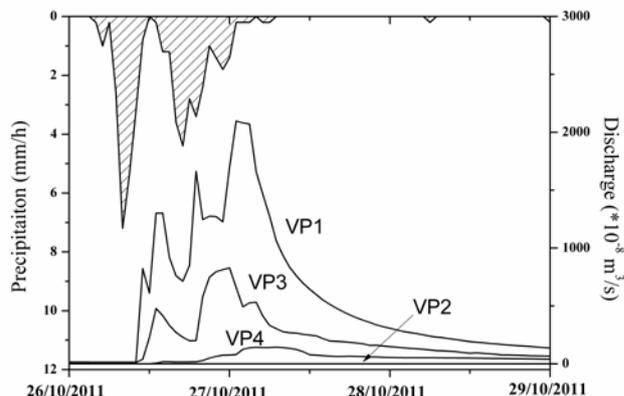


Figure 3. Different response of each drip to a rain event from 26th to 27th, October 2011.

4. RESULTS

4.1. The hydrology of four drips

The four permanent drips in the cave showed different hydrological performances. An example of drip reaction to precipitation a slight rainfall at the end of October is illustrated, with a total amount of 46.4mm rainfall fallen from 26th to 27th, October 2011 (Fig. 3). According to the speed and intensity in response to the precipitation, each drip could be described as: “rapid response with high intensity discharge” (VP1); “rapid response with moderate discharge” (VP3); “rapid response with negligible discharge” (VP4) and “no response” (VP2). VP1 had rapid response to the precipitation, with a high fast discharge flow followed by a long subsiding period. There was no apparent response from VP2 to the event. VP3 and VP4 responded fast while they had lower discharges. This suggested that VP1 showed the greatest sensitivity to catch the signal of surface weather change, which also represented the fast flow, while VP2 represented seepage flow through the epikarst. In some dry periods, only VP1 showed a response to the rain events, but the VP2 only had limited response after the diffusion events. Thus, both drips were selected in order to analyse and compare the water chemistry.

4.2. The seasonal environment variation

In the study area, August is the hottest time of the year and December is usually cold and wet. In August, with high temperatures and high evaporation, discharge from the drips was very low. During this period, the rain fall commonly came as short but intense storms, which are the so called “concentrated rain”. To the contrary, in a period of colder conditions (e.g. December), the rainfall fell more lightly but frequently. The study of VP1 was carried out in the period when the outside temperature declined (Fig. 4). As a result of different temperature and precipitation performance, the study period could be divided into two parts. Prior to the rain event VP1-OCT1, the precipitation fell as a short intensive storm, namely concentrated rainfall. Most of these rain events were insufficiently intensive for the efficient recharge of the underground system. But after event VP1-OCT1, the diffuse rains fell gently and were sustained over time, which recharged the epikarst efficiently (Fig. 4).

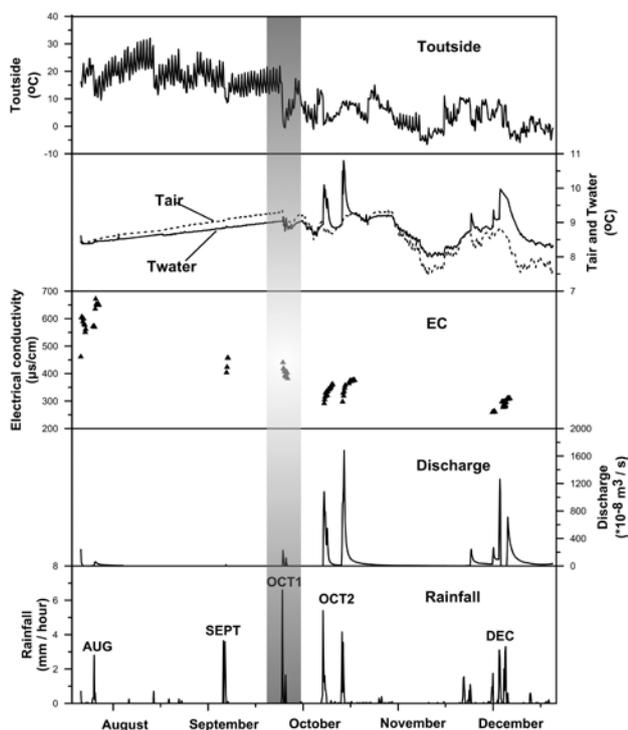


Figure 4. Air temperature at the surface and near drip VP1, temperature, EC and discharge of the drip water (VP1), discharge of VP1 and rainfall for the entire period (August 4th to December 31st 2011). The shadow indicates the division of the study period.

Several intensive rain events occurred over the study period of VP1, but only five of them supplied the drips efficiently: from 4th to 9th of August 2011 with 42.8 mm rainfall (hereafter as VP1-AUG), on 19th September 2011 with 47.4 mm (VP1-SEPT), from 7th to 9th October 2011 with 42.8 mm

(VP1-OCT 1), from 18th to 27th October 2011 with 105 mm (VP1-OCT 2) and from 13th to 18th December with 92 mm (VP1-DEC). As VP2 showed only weak response to the rain events, a single proper event was selected for comparison, which was from 28th November to 2nd December 2012 with 74.2mm (VP2-NOV).

4.3. Responses of hydrochemistry to rain events

The main ions in the drip water from both sites were Ca^{2+} , Mg^{2+} , and HCO_3^- (Table 1). As the outside temperature became cooler, they also decreased and synchronized downward with electrical conductivity (EC). From August to December, the EC decreased gradually, from 589 $\mu\text{s}/\text{cm}$ to 294 $\mu\text{s}/\text{cm}$ (VP1).

Accompanied by the variation in discharge as a response to rain patterns, the EC also showed a relevant response. During the concentrated rainfall period (the time before VP1-OCT1, Fig. 4), the drips generally stopped when the rainfall ceased. With regard to the variation in EC, when the discharge increased to the highest value, a fall of EC was synchronous. Following the fastest flow the EC increased rapidly to its maximum, then it decreased slowly until the drip water ceased. Such response was observed in VP1-AUG, VP1-SEPT and VP1-OCT1, though the event VP1-SEPT was too short to present its peak.

After entering the diffuse rain period (the time after VP1-OCT2, Fig. 4), the drip water always maintained a detectable flow, resulting in the different response in EC (Fig. 5). Similar to the previous period, EC decreased immediately after the discharge peaks. However, after the trough, the EC rose gradually until it arrived at a stable value. Such responses were observed in VP1-OCT2, and in VP1-DEC (Fig. 5).

The rain event VP2-NOV occurred as diffuse rain, which resulted some response of drip VP2. A small amount of fast flow resulted in the low EC at the beginning of the rain event at VP2, while it rose up rapidly as the main flow came. Subsequently, as the discharge decreased, EC also declined into a stable value (VP2-NOV, Fig. 5), which was different from the VP1.

4.4. The Mg/Ca ratio as a response to rain events

The Mg/Ca ratio of drip water had distinct seasonal variation reflecting different rain patterns (Fig. 6).

Table 1 Chemical data on drip water VP1 and VP2 during the research period.

Rain event	Sample type	pH	pCO ₂ (log10)	Cl ⁻ (mg l ⁻¹)	NO ₃ ⁻ (mg l ⁻¹)	SO ₄ ²⁻ (mg l ⁻¹)	Na ⁺ (mg l ⁻¹)	K ⁺ (mg l ⁻¹)	Ca ²⁺ (mg l ⁻¹)	Mg ²⁺ (mg l ⁻¹)	HCO ₃ ⁻ (mg l ⁻¹)	SIc	Mg/Ca (×10 ³ molar)
VP1-AUG(10*)	Average	8.33	-2.78	0.43	1.01	1.17	0.54	0.31	73.88	50.15	478.98	1.08	1.23
	σ	0.02	0.05	0.14	0.44	0.24	0.11	0.14	19.69	6.87	65.71	0.17	0.47
	Max	8.35	-2.73	0.81	1.84	1.77	0.86	0.68	101.59	61.12	585.59	1.32	2.67
	Min	8.30	-2.86	0.31	0.33	0.96	0.47	0.20	42.03	36.38	405.74	0.83	0.85
VP1-SEPT(4)	Average	8.36	-2.94	1.47	3.14	2.21	0.44	0.48	66.56	29.60	347.47	0.99	0.74
	σ	0.01	0.02	0.04	1.62	0.08	0.04	0.20	3.69	1.20	18.72	0.04	0.01
	Max	8.36	-2.92	1.52	5.55	2.33	0.48	0.69	70.68	30.73	367.66	1.03	0.76
	Min	8.35	-2.96	1.43	2.06	2.15	0.38	0.28	63.00	28.48	329.50	0.95	0.72
VP1-OCT 1(13)	Average	8.38	-2.97	0.55	2.70	1.43	0.43	0.22	62.12	31.23	344.64	0.98	0.84
	σ	0.01	0.02	0.25	1.65	0.39	0.03	0.19	4.29	1.66	15.32	0.04	0.07
	Max	8.39	-2.93	1.25	7.46	2.59	0.48	0.84	69.43	33.29	367.29	1.03	0.95
	Min	8.37	-3.01	0.32	1.24	1.09	0.39	0.12	55.16	27.74	321.56	0.91	0.75
VP1-OCT 2(21)	Average	8.37	-3.04	0.44	1.14	1.02	0.37	0.15	52.69	24.16	281.64	0.84	0.76
	σ	0.06	0.06	0.18	0.41	0.13	0.05	0.07	5.08	3.05	30.10	0.10	0.04
	Max	8.44	-2.93	0.74	1.65	1.21	0.44	0.31	59.42	28.67	321.35	0.99	0.87
	Min	8.24	-3.13	0.26	0.40	0.74	0.29	0.09	44.86	19.23	233.91	0.59	0.71
VP1-DEC(15)	Average	8.35	-3.10	0.84	1.11	1.31	0.37	0.17	40.72	21.97	232.87	0.64	0.75
	σ	0.06	0.07	0.29	0.45	0.09	0.05	0.10	5.12	4.50	15.30	0.07	0.01
	Max	8.42	-2.92	1.33	1.83	1.50	0.44	0.47	46.78	29.34	249.14	0.76	0.77
	Min	8.20	-3.18	0.47	0.50	1.21	0.29	0.09	32.30	17.23	203.79	0.41	0.73
VP2-NOV(8)	Average	8.17	-2.56	1.34	0.40	2.30	0.87	0.43	62.73	54.14	463.88	0.93	2.26
	σ	0.07	0.09	0.20	0.10	0.24	0.11	0.08	10.13	2.18	38.90	0.10	0.09
	Max	8.28	-2.42	1.81	0.60	2.80	1.11	0.55	76.18	57.88	523.65	1.06	2.41
	Min	8.06	-2.70	1.19	0.31	2.08	0.76	0.33	45.88	51.54	404.55	0.80	2.15

*: number of samples; EC: electrical conductivity; σ: standard deviation.

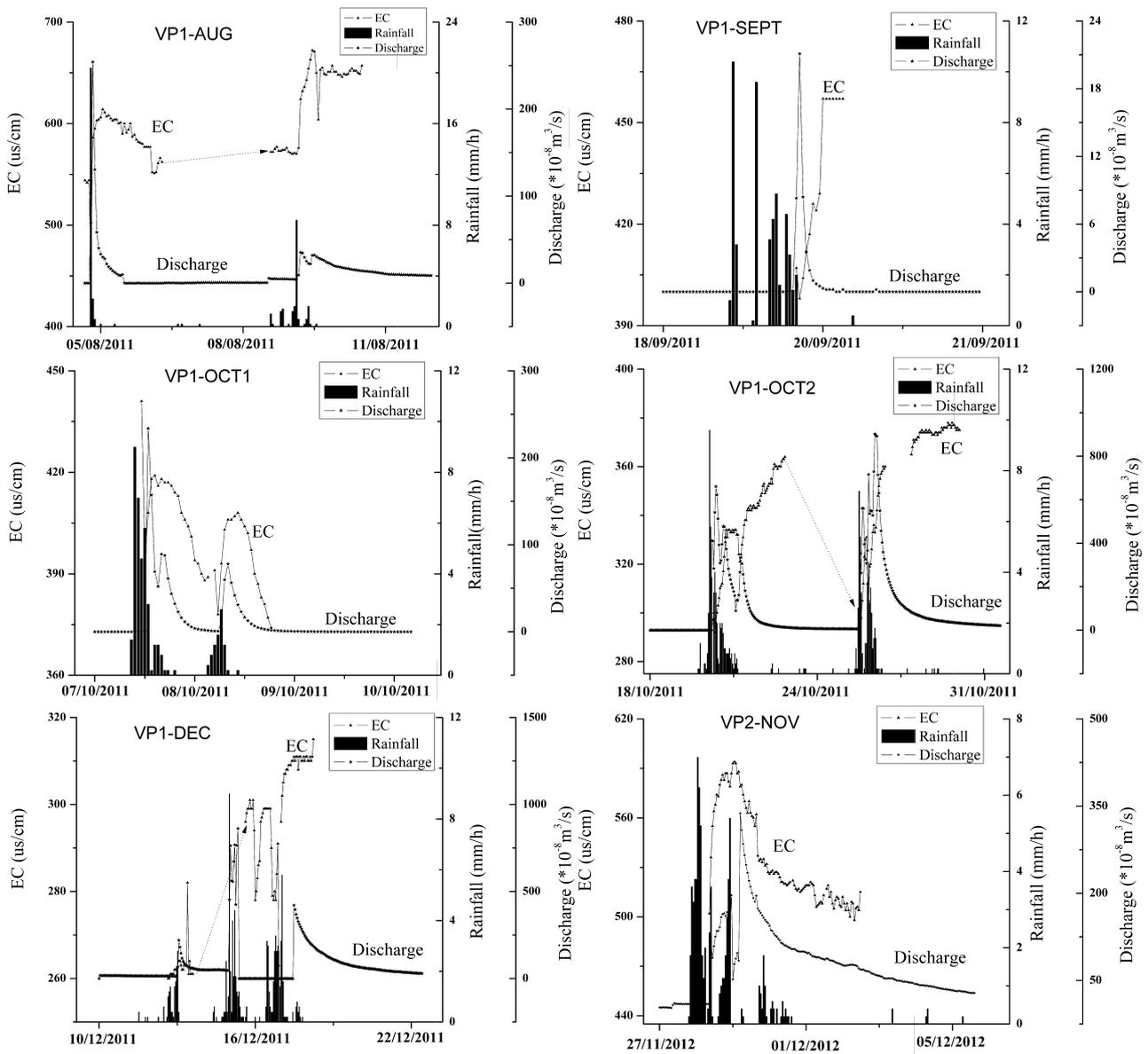


Figure 5. The precipitation and the relevant discharge and electrical conductivity of drip VP1 during the five main rain events in 2011 and drip VP2 in 2012.

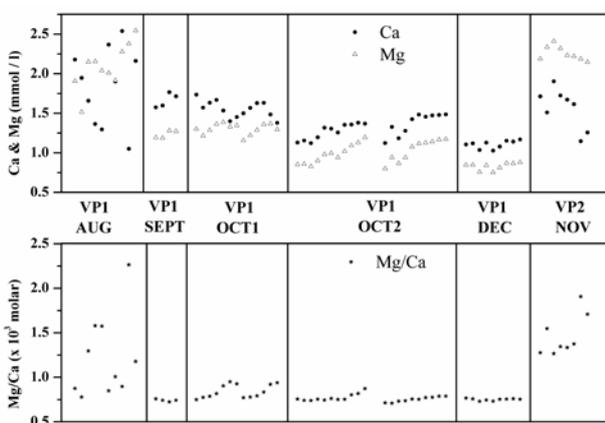


Figure 6. The Mg/Ca ratio and concentration of Ca^{2+} and Mg^{2+} in the drip water of VP1 and VP2 during the research period.

Both Ca^{2+} and Mg^{2+} ion concentrations have a similar variation pattern as the Mg/Ca ratio, while they decreased as the season changed. During August, the Mg/Ca ratio varied randomly, and with a high value (range from 0.85 to 2.27). After that, the variation of Mg/Ca ratio smoothed out. During the concentrated rainfall period, The Mg/Ca ratio was low when the rain commenced while it increased slightly at the end of each storm (Fig. 6). After entering the diffuse rain period, the concentration of Ca^{2+} and Mg^{2+} slightly rose at the end of each storm, but their ratio remained stable. The Mg/Ca ratio kept a low and stable value which was prolonged into VP1-DEC, with Mg/Ca ratio at about 0.75. However, the ratio at VP2 was higher and more random than at VP1 during the diffuse rain period (November).

5. DISCUSSIONS

5.1. Different response of EC to different rain patterns

In the Velika Pasica Cave, the EC of VP1 expressed characteristic responses to two different rainfall patterns. During the concentrated rain fall period, the discharge had the peak value after the intensive rainfall, meanwhile the EC had a quick fall (Fig. 5) in response to the dilution effect (Baldini et al., 2006; Liu et al., 2007; McDonald & Drysdale, 2007). After the peak flow, the water flow slowed down. The water in epikarst with a high CO₂ content, coming from the soil layer, reacted efficiently with the bedrock. This resulted in the steep rise in EC as a consequence of dissolution of the major ions. However, the hot, dry weather resulted in the shallow epikarst water evaporating intensively, which aggravated the flow decline. Without further water supply, the CO₂ of the water in the epikarst was consumed quickly, which was represented by the EC value. The EC value of the drip water had a gentle declination until the drip ceased. The phenomenon is explained as the process of slow flow dissolution. During this dry condition, without sufficient water supplement, the CO₂ affect was one of the controlling impacts on the hydrochemistry of karst water, similarly discussed by Zhang et al., (2011) from an epikarst spring in Chongqing. This situation lasted till the rain event VP1-OCT2, when the temperature dropped and the rain pattern altered.

The events after VP1-OCT2 (Fig. 5) were characterised as diffuse rainfall, starting gently and lasting much longer. With the different rain patterns, the discharge never ceased. When the rain commenced, the drip water was mainly supplied by the conduit flow, which had fast response to the rainfall (Liu & Brancelj, 2011). When the fast flow ceased, the fracture-net became the major source for the drip water. The infiltrated water had slow access to an extended rock surface and reacted efficiently there, resulting in the sharp EC increase. The flow continued to slow down, but it remained at a detectable level. As a result, the EC stayed at a stable value, as the CO₂ can be supplied sufficiently and continuously, and it had enough time to reach the dissolution equilibrium. Since the fractures were already filled with water, when the second storm came, the rain water affected the drip water more quickly and directly. This happened similarly in VP1-DEC (Fig. 5).

However, the dilution effect was less functional in VP2, and the piston effect was principal here (Tooth & Fairchild, 2003, Frenández-Cortès et

al., 2008). The highest EC was relevant to the main discharge, which represented the upper 'new' water pushing the 'old' water slowly downward to discharge.

In summary, the comparison of the hydrochemical profiles of different drips represented the dual-medium vadose structure of epikarst (Atkinson, 1977; Liedl et al., 2003). It is not hard to find that at least two key processes were controlling hydrochemical variations: (i) the retention time of epikarst water; (ii) the gas-water-rock interactions (CO₂). The former mainly corresponds to the speed of water flow, while the later predominantly relied on the dissolve ability.

Over the measurement period, the EC decreased gradually from August to December, and the range in the EC variation became smaller. The pCO₂ showed a similar depression which indicated an important role of CO₂ concentration to EC. The concentration of CO₂ was mainly controlled by the influence of seasonal climate change on the vegetation growth and soil biological activity, which controlled the intensity of karst processes (Yang et al., 2012).

5.2. The Mg/Ca ratio

Ca²⁺ and Mg²⁺ have the similar variation to the Mg/Ca ratio, but not exactly similar as other caves (Baldini et al., 2006; Fairchild et al., 2006). Several factors can affect the cation concentrations in the cave drip water, and these may act independently or in synergy (Verheyden et al., 2000). Different types of rain patterns and the structure of the epikarst were the significant factors for the variation in the Mg/Ca ratio (Fig. 6), which resulted in different patterns of water flow in the epikarst (Liu & Brancelj, 2011).

As to VP1, during the concentrated rainfall period, when the fast flow arrived, it did not have sufficient time to react in the vadose zone. Later, when the slow flow began to prevail, the water could flow much longer within the matrix and react more efficiently. Prior Calcite Precipitation (PCP) along the flow path resulted in the decrease of Ca²⁺, and the increase of Mg/Ca ratio at the end of each rain event (Huang et al., 2001; Tooth & Fairchild, 2003). During the diffuse rainfall period, with frequent rain water supplement, the drip water kept detectable water flow, which was replaced continuously, thus the PCP rarely works here, as indicated by the low but stable Mg/Ca ratio. However, from the variation in VP2, the slow water responded as a piston, which resulted in a higher Mg/Ca ratio. Thus, the Mg/Ca ratio in the drip water was affected significantly by the retention time in the epikarst/vadose zone.

6. CONCLUSIONS

The transformation from rain water to cave drip water occurs over a relatively short distance and within a short time span with significant changes in ion content (three major ions: Ca^{2+} , Mg^{2+} and HCO_3^-) reflected in differences in EC. Because of the high correlation between these main ions and EC, the high resolution monitoring of hydrochemical variation could be conducted. From the discussion above, the different rain patterns occurred as concentrated rainfall and diffuse rainfall, were one of the principal impacts on the hydrochemical composition of the cave drip water, which corresponded to the seasonal variation from August to December at VP1. Induced by the different rain intensity and patterns, the time profile of the EC at VP1 had two characteristics: i) it had an obvious response to the dilution effect whenever intensive rainfall occurred; ii) After the fast flow of the concentrated rain events, it has a process of slow flow dissolution, with decreased EC; while during the diffuse rain events, it can arrive at the dissolution equilibrium, rising to a stable EC. In comparison with VP2, due to the seepage flow, the high EC synchronized with the high discharge as piston driven. Meanwhile, Mg/Ca ratio in cave drip water shows a distinct pattern over time, affected by the prior calcite precipitation (PCP) effect resulted from different rain patterns. All of these infer the resident time of the drip water in epikarst affects its hydrochemical profile, while the rain pattern was an important impact. As a reflection of the complexity of the epikarst system, the impact factors on hydrochemical variation of drip water were various, e.g. the temperature, the depth of surface soil layer, the structure of epikarst et al rain patterns but further discussion on other impacts, such as the temperature and the relative humidity, will be conducted. The discussion here focused on the

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REFERENCES

- Appelo, C.A.J. & Postma, D., 2005. *Geochemistry groundwater and pollution (Version 2)*. Taylor & Francis, 683.
- Atkinson, T.C., 1977. *Diffuse flow and conduit flow in limestone terrain in the Mendip Hills, Somerset (Great Britain)*. Journal of Hydrology, 35, 93-110.
- Baker, A., Barnes, W.L. & Smart P.L., 1997. *Variations in the discharge and organic matter of stalagmite drip waters in Lower Cave, Bristol*. Hydrological Processes, 11, 1541-1555.
- Baker, A., & Brundson C., 2003. *Non-linearities in drip water hydrology: an example from Stump Cross Cavern, Yorkshire*. Journal of Hydrology, 277, 151-163.
- Baker, A., Genty, D. & Fairchild, I.J., 2000. *Hydrological characterization of stalagmite drip waters at Grotte de Villars, Dordogne, by the analysis of inorganic species and luminescent organic matter*. Hydrology and Earth System Sciences, 4, 3, 439-449.
- Baldini, J.U.L., McDermott, F. & Fairchild, I.J., 2006. *Spatial variability in cave drip water hydrochemistry: implications for stalagmite paleoclimate records*. Chemical Geology, 235, 3-4, 390-404.
- Brancelj, A., 2002. *Microdistribution and high diversity of copepoda (Crustacea) in a small cave in central Slovenia*. Hydrobiology, 477, 59-72.
- Fairchild, I.J., Tuckwell, G.W., Baker, A. & Tooth, A.F., 2006. *Modelling of dripwater hydrology and hydrochemistry in a weakly karstified aquifer (Bath, UK): implications for climate change studies*. Journal of Hydrology, 321, 1-4, 213-231.
- Frenández-Cortès, A., Calaforra, J.M. & Sánchez-Martos, F., 2008. *Hydrogeochemical processes as environmental indicators in drip water: Study of the Cueva del Agua (Southern Spain)*. International Journal of Speleology, 37, 1, 41-52.
- Genty, D. & Deflandre, G., 1998. *Drip flow variations under a stalactite of the Père Noel cave (Belgium)*. Journal of Hydrology, 211, 208-232.
- Huang, Y., Fairchild, I.J., Borsato, A., Frisia, S., Cassidy, N.J., McDermott, F. & Hawkesworth, C.J., 2001. *Seasonal variations in Sr, Mg and P in modern speleothems (Grotta di Ernesto, Italy)*. Chemical Geology, 175, 3-4, 429-448.
- Hu, C.Y., Henderson, G.M., Huang, J.H., Chen, Z.H., & Johnson, K.R., 2008. *Report of a three-year monitoring programme at Heshang Cave, Central China*. International Journal of Speleology, 37, 3, 143-151.
- Liedl, R., Sauter, M., Huckinghaus, D., Clemens, T. & Teutsch, G., 2003. *Simulation of the development of karst aquifers using a coupled continuum pipe flow model*. Water Resource Research, 39, 3, 1057-1062.
- Liu, A.W. & Brancelj, A., 2011. *Response of cave drip water to different recorded rainfall patterns in Velika Pasjica cave, central Slovenia*. In Bertrand, C., (ed). Proceeding of H2karst, 9th Conference on

Limestone Hydrogeology, 307-310.

- Liu, Z.H., Li, Q., Sun, H.L. & Wang, J.L., 2007.** *Seasonal, diurnal and storm-scale hydrochemical variations of typical epikarst springs in subtropical karst areas of SW China: soil CO₂ and dilution effects.* Journal of Hydrology, 337, 1-2, 207-223.
- McDonald, J. & Drysdale, R., 2007.** *Hydrology of cave drip waters at varying bedrock depths from a karst system in southeastern Australia.* Hydrological Processes, 21, 1737-1748.
- Pleničar, M., 1970.** *Tolmačk Osnovni geološki karti SFRJ, List Postojna. Zvezni geološki zavod Beograd.* Basic geological survey; section Postojna, 62.
- Tooth, A.F. & Fairchild, I.J., 2003.** *Soil and karst hydrological controls on the chemical evolution of speleothem-forming drip waters, Crag Cave, southwest Ireland.* Journal of Hydrology, 273, 1-4, 51-68.
- Verheyden, S., Keppens, E., Fairchild, I.J., McDermott, F. & Weis, D., 2000.** *Mg, Sr and Sr isotope geochemistry of a Belgian Holocene speleothem: implications for paleoclimate reconstructions.* Chemical Geology, 169, 131-144.
- Yang, R., Liu, Z.H., Cheng Zeng, C. & Zhao, M., 2012.** *Response of epikarst hydrochemical changes to soil CO₂ and weather conditions at Chenqi, Puding, SW China.* Journal of Hydrology, 468-469, 151-158.
- Zhang, C., Yan, J., Pei, J.G. & Jiang, Y.J., 2011.** *Hydrochemical variations of epikarst springs in vertical climate zones: a case study in Jinfo Mountain National Nature Reserve of China.* Environmental Earth Sciences, 63, 2, 375-381. doi: 10.1007/s12665-010-0708-y

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