Journal of Climate Change, Vol. 2, No. 2 (2016), pp. 89–98.
DOI 10.3233/JCC-160020

Monsoon Climate Impact on Drip Water Geochemistry at Niah Great Cave, NW Borneo, Malaysia: Evaluating the Spatial and Temporal Trends

M.V. Prasanna[1]*, S. Chidambaram[2], R. Nagarajan[1] and A. Anand Kumar[1]

[1]Department of Applied Geology, Faculty of Engineering and Science, Curtin University Sarawak
CDT 250, 98009 Miri, Sarawak, Malaysia
[2]Department of Earth Sciences, Annamalai University, Annamalai Nagar – 608002, India
✉ geoprasanna@gmail.com

Received March 3, 2016; revised and accepted May 24, 2016

Abstract: A total of nine drip water samples were collected at Trader Cave Entrance (TCE), Cave Center (CC) and Painted Cave Entrance (PCE) of Niah Great Cave, NW Borneo, Malaysia during monsoon period to understand the spatial and temporal variations of drip water geochemistry by comparing with the summer season data. The collected samples were analyzed for physico-chemical parameters using standard procedures. The chemical components of the limestone host rock indicate that its dominant mineral component is low magnesium calcite. Interpretation of data shows that higher ionic concentration was noted in TCE followed by CC and PCE in monsoon. However the ionic concentration in summer season was much higher than the monsoon season. Ca-HCO_3 is the most common water type recognized in the study site which indicates the carbonate dissolution by water-rock interaction. Higher ionic strength values were noted in TCE drip waters indicating high flushing rate of recharge water, which released more ions into the drip water. The saturation index of calcite and aragonite are in near saturation to over saturation state, whereas magnesite and dolomite are under saturation condition. The results of factor analysis reveal that the geochemistry of drip water is mainly controlled by the carbonate mineral–water equilibrium.

Keywords: Drip water, Geochemistry, Seasonal variation, log pCO_2, Saturation index.

Introduction

The hydrogeochemical characteristics of cave waters in karst environment are mainly controlled by the water-rock interaction in carbonate rocks (Ford and Williams, 2007). The hydrogeochemistry of cave waters is easily influenced by the environmental changes due to the similar hydrogeological structures (Yuan, 1997). Hence, a systemic study on hydrogeochemistry of cave waters is needed to understand the karst processes (Yoshimura et al., 2001; Han and Liu, 2004), evolution of karst landforms (Kaufmann, 2009; Mocochain et al., 2009), environmental changes (Xiao and Weng, 2007; Ducci et al., 2008) and global carbon fluxes (Liu et al., 2008; Hagedorn and Cartwright, 2009).

Karst system is a crucial interface between seepage water and fractured carbonate rocks. In the karst environment, CO_2 originates mainly from pedogenic processes through the hydration of water and then ionizing CO_2 within the humic topsoil (Dreybrodt, 1988). When the seepage water reaches the carbonate rock, this carbonic acid dissolves the carbonate minerals

*Corresponding Author

that can be explained by the equation: $CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$. The seepage water is in thermodynamically equilibrium with the soil atmosphere within the fractured unsaturated zone. Since the cave system is generally open to the outer CO_2 poor atmosphere, the water reaching the cave atmosphere has a tendency and precipitating the solid carbonate that forms speleothems. Calcium content in the drip water changes in pCO_2 in the cave and their effect on carbonate saturation are the important factors for the calcite precipitation (Fairchild et al., 2006; Fairchild and McMillan, 2007). The various geochemical processes like prior calcite precipitation, dilution, piston flow etc. are controlling the chemistry of drip water in a cave as response to different hydrological conditions to rainfall (Tooth and Fairchild, 2003). Percolation of rainwater into a cave system is a diphasic flow of water and CO_2 influence (Atkinson, 1977). Evapotranspiration and geochemical evolution of water depend on the soil, unsaturated zone and on the transit time.

The seasonal evolution of the water flow within the cave system depends on the rainfall as an original input and also contributes to runoff of sinking stream into the karst system. Environmental parameters of the caves, like humidity and temperature depend upon the entrance of water into the cavity. The infiltration of low-pH rainwater into groundwater that incorporated atmospheric CO_2 as well as CO_2 from the near-surface environment and these initial CO_2 concentrations which dictate the amount of limestone dissolution (White, 1988). Continuous input of meteoric water charged with atmospheric and soil CO_2 enters the vadose zone to keep this water under-saturated with respect to $CaCO_3$ and thereby maintain its dissolution potential.

Studies conducted at various seasons or water-balanced cycles show significant intra and inter site variability in drip water hydrochemistry (Baker et al., 2000; Tooth and Fairchild, 2003; McDonald et al., 2004; Spotl et al., 2005; Baldini et al., 2006; Johnson et al., 2006). A preliminary study was conducted in Niah Great Cave during July 2011 to understand the geochemical behaviour of drip waters in dry period (Prasanna et al., 2014). There is no detailed study on spatial and temporal variations in drip water geochemistry of Niah cave. Hence, the main objective of this study is to understand the monsoonal impacts on drip water geochemistry and to evaluate the spatial and temporal trends in Niah Great Cave.

Study Area

Niah Great Cave is located in Sarawak, NW of Borneo, east Malaysia (Figure 1). It has been developed in the algal patch reef facies of the Subis Limestone Member of the Tangap Formation, of Miocene age. This formation consists of calcareous shale, marl, greenish claystone, and pure limestone beds (Hutchinson, 2005). In this cave, about 3200 m of passages have been identified which includes chambers up to 100 m in diameter and 70 m high. The morphology of the cave passages, with Scallops features, is consistent with the cave being of phreatic origin (Hunt and Rushworth, 2005a, b). The climate of Sarawak is warm and humid throughout the year. The mean annual temperature at sea level is about 27ºC with a lapse rate of 0.5–0.7ºC/100 m elevation. The average annual rainfall is about 2813.5 mm per year (Niah Forest Office). Higher rainfall is recorded during the month of December and lesser in June.

Methodology

Nine drip water samples were collected at different sites in Niah Great Cave in order to spatially cover the entire cave (three samples in TCE, five samples in CC and one sample in PCE) during February 2015 (Figure 1). The samples were mainly collected from the fractures and fissures of cave ceiling. The collected samples were analyzed for various chemical parameters using standard methods described in APHA (1995). Temperature, pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured in the field using portable pH and conductivity meter (Thermo Scientific Orion Star, 4 Star Plus Meter). The samples were collected in 250 ml polyethylene bottles and kept at a temperature of 4°C until analysis. The collected samples were filtered using a preconditioned plastic Millipore filter unit equipped with a 0.45 µm filter membrane for further elemental analysis. Bicarbonate (HCO_3^-) and chloride (Cl^-) were measured using titrimetric method. Sulfate (SO_4^{2-}) were analyzed using Hack Test Kits (SulfaVer 4 method). The collected samples were preserved by acidifying to pH ~2 with HNO_3 for calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+) were analysed using Atomic Absorption Spectrophotometer (Perkin Elmer Analyst 400). The precision of analysis was checked by error percentage calculation and it is found to vary between ±1 to ±10% (Hem, 1985). A representative limestone host rock sample was collected in the Cave and subjected to XRF analysis using Axios PANalytical X-ray fluorescence (XRF) machine. Ionic strength

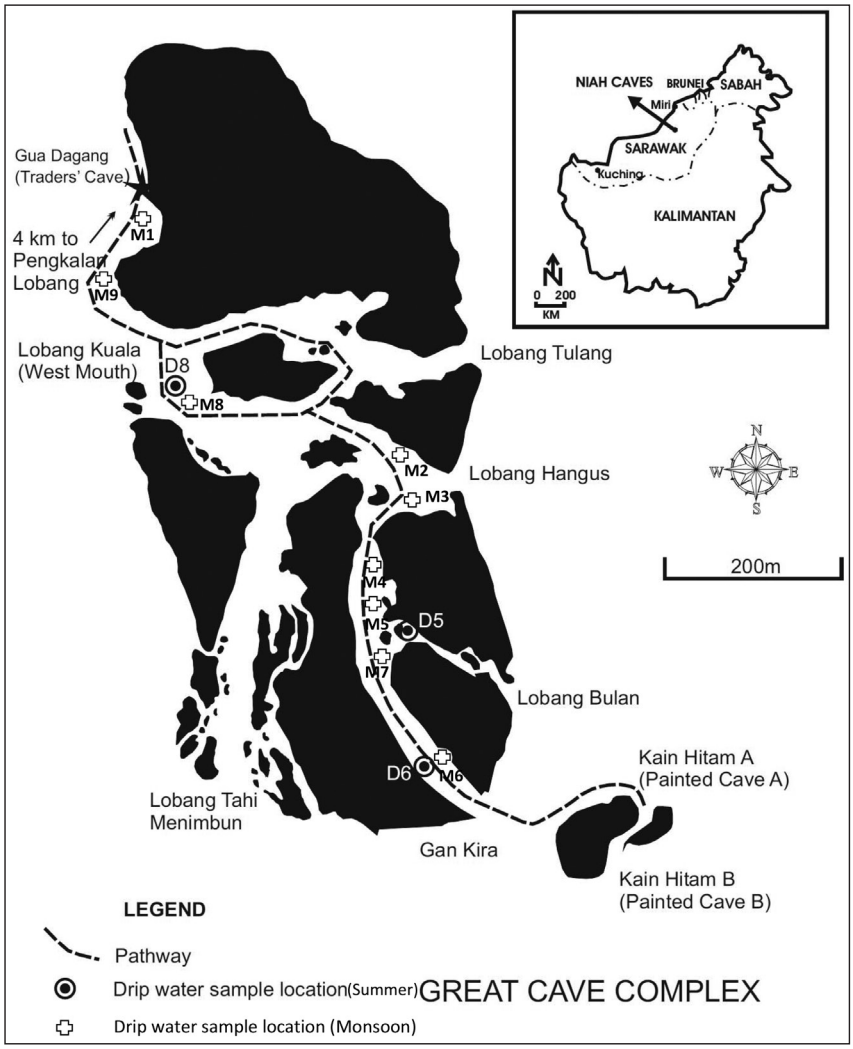

Figure 1: Study area with sample location sites (modified from Prasanna et al., 2014).

(IS), carbon dioxide partial pressure (log pCO_2) and saturation index (SI) of carbonate minerals were computed using the WATEQ4F (Ball and Nordstrom, 1992). Factor analysis was performed using SPSS software (version 17 for Windows).

Results and Discussion

Chemical Composition and Mineralogy of Host Rock

A representative host rock sample was chosen for the chemical component analysis using XRF method to characterize the chemical composition and to provide support to the inference about the mineral compositions of the host rock by XRD method. The results of XRD indicated the presence of large amount of calcite, particularly Rhombohedral calcite, in the host rock (Prasanna et al., 2014). The results of XRF show that Ca and Mg contents were higher than the other elements (Figure 2). Besides Ca and Mg, other components are much lower in the rock. In general, calcites have a magnesium carbonate molar ratio of less than 4% (Mg/Ca < 4) and can be classified as the low magnesium calcite (LMC) (Stanley et al., 2002). The Ca and Mg molar ratio of the limestone host rock sample was 0.33%

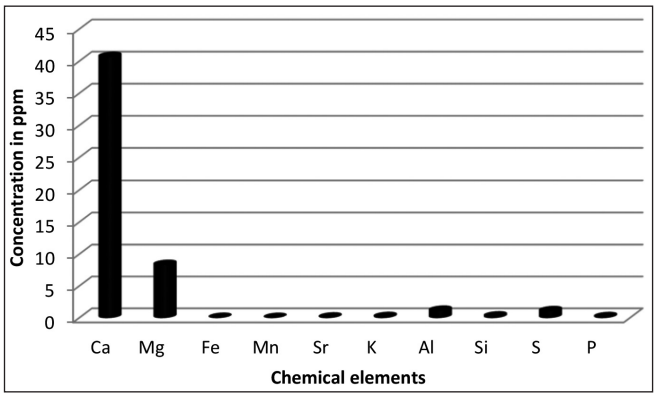

Figure 2: The chemical composition of host rock.

which shows that the dominant carbonate minerals belong to LMC, which is consistent with the observation about the mineral composition of host rock.

Trends of Environmental Parameters and Major Ions in Drip Waters

The chemical composition of drip waters collected at TCE, CC and PCE are given in Table 1. The temperature does not change much seasonally, and all the samples range from 24.98ºC to 25.26ºC irrespective of seasons. The other environmental parameters are quite variable in different locations and seasons. In monsoon, pH ranges from 7.90 to 8.52 with an average of 8.15 in TCE, 8.05 to 8.31 with an average of 8.21 in CC and 8.13 in PCE. Higher pH was observed in CC followed by TCE and PCE. In summer, pH ranges from 6.65 to 6.92 with an average of 6.79 and higher pH was noted in PCE followed by TCE and CC. Overall, the pH values show alkaline nature in monsoon period, whereas near acidic to neutral condition in summer period. In monsoon, EC ranges from 171.99 µs/cm to 187.51 µs/cm with an average of 178.32 µs/cm in TCE, 142.64 µs/cm to 173.79 µs/cm with an average of 155.71 µs/cm in CC and 133.25 µs/cm in PCE. Higher EC was observed in TCE, followed by CC and PCE. In summer, EC ranges from 207.60 µs/cm to 774 µs/cm with an average of 460.53 µs/cm and it shows the same trend of monsoon. In general, the EC values are lower in monsoon season compared to summer season.

In general, Ca^{2+} and HCO_3^- are the predominant cation and anion in karst waters (Yuan et al., 2002; Ford and Williams, 2007) and for the drip waters in Niah Cave is also the same condition irrespective of seasons. Based on the average values of all chemical parameters in these three localities, higher ionic concentrations was observed in TCE, followed by CC and PCE (Figure 2). Same trend has been observed in summer season samples (Prasanna et al., 2014), but higher ionic concentrations was recorded than monsoon season. The order of dominance of major ions are Ca^{2+}> K^+> Na^+> Mg^{2+} = HCO_3^->Cl^-> SO_4^{2-} in TCE; Ca^{2+}>Na^+> Mg^{2+}> K^+ = HCO_3^->Cl^-> SO_4^{2-} in CC; Ca^{2+}> Mg^{2+}> Na^+> K^+ = HCO_3^->Cl^-> SO_4^{2-} in PCE. The concentration of Ca^{2+} ranges from 45.16 mg/l to 139.49 mg/l with an average of 87.33 mg/l in summer and it ranges from 28.15 mg/l to 64.9 mg/l with an average of 41 mg/l in monsoon. HCO_3^- ranges from 73.20 mg/l to 85.40 mg/l with an average of 77.27 mg/l in summer and it ranges from 73.2 mg/l to 122 mg/l with an average of 94.21 mg/l in monsoon. In general, Ca^{2+} and HCO_3^- in the drip waters show a clear seasonal variation, the concentration of which is higher in summer than that of monsoon. It is also interesting to note that there is a spatial trend observed in summer season (Figure 3). Mg^{2+} concentration also shows remarkable seasonal variation, where the values are higher in summer than monsoon season. Chloride content shows an increasing trend in summer and probably derived from the atmospheric input (Mayer, 1999).

The chemical behaviour of drip waters in Niah Cave have been compared with few other caves in the world in various karst environments (Table 2). This review of the literature shows that Ca^{2+} and Mg^{2+} concentration of drip waters in Niah cave during monsoon period is less

Table 1: Chemical composition of drip waters (all values in mg/l except EC in µs/cm, temperature in °C and pH)

Sample ID	*Location*	*Drip rate*	*Temp*	*pH*	*TDS*	*EC*	*Ca^{2+}*	*K^+*	*Mg^{2+}*	*Cl^-*	*HCO_3^-*	*SO_4^{2-}*	*Na^+*
M 1	TCE	Fast	25.4	8.5	187.5	267.9	46.3	0.2	1.0	12.0	122	3.6	2.5
M 2	CC	Slow	24.8	8.3	173.8	248.3	64.9	1.8	2.4	16.0	73.2	11.0	4.5
M 3	CC	Fast	25.3	8.3	157.2	224.6	35.1	0.7	0.6	8.0	97.6	10.0	5.2
M 4	CC	Fast	24.7	8.2	152.2	217.4	31.2	0.6	1.4	12.0	91.5	11.5	4.1
M 5	CC	Slow	24.6	8.2	152.7	218.2	35.9	0.5	1.3	12.0	85.4	12.0	5.7
M 6	PCE	Slow	24.4	8.1	133.3	190.4	32.3	0.7	1.8	16.0	79.3	2.0	1.1
M 7	CC	Fast	24.8	8.1	142.6	203.8	28.2	0.6	1.2	8.0	91.5	9.0	4.2
M 8	TCE	Fast	25.4	8.0	172.0	245.7	57.2	9.3	5.0	12.0	85.4	1.0	2.1
M 9	TCE	Fast	25.4	7.9	175.4	250.6	38.1	0.2	0.8	8.0	122	3.2	3.1
*D5	CC	Slow	25.4	6.7	173.1	400.0	77.3	2.7	0.4	4.5	73.2	10.1	3.1
*D6	PCE	Fast	25.3	6.9	153.8	207.6	45.2	2.7	0.02	2.3	85.4	2.5	1.3
*D8	TCE	Fast	25.1	6.8	240.7	774.0	139.5	8.5	0.5	5.9	73.2	7.9	2.9

*Summer season data (Prasanna et al., 2014); TCE – Trader cave entrance, CC – Cave center, PCE – Painted cave entrance.

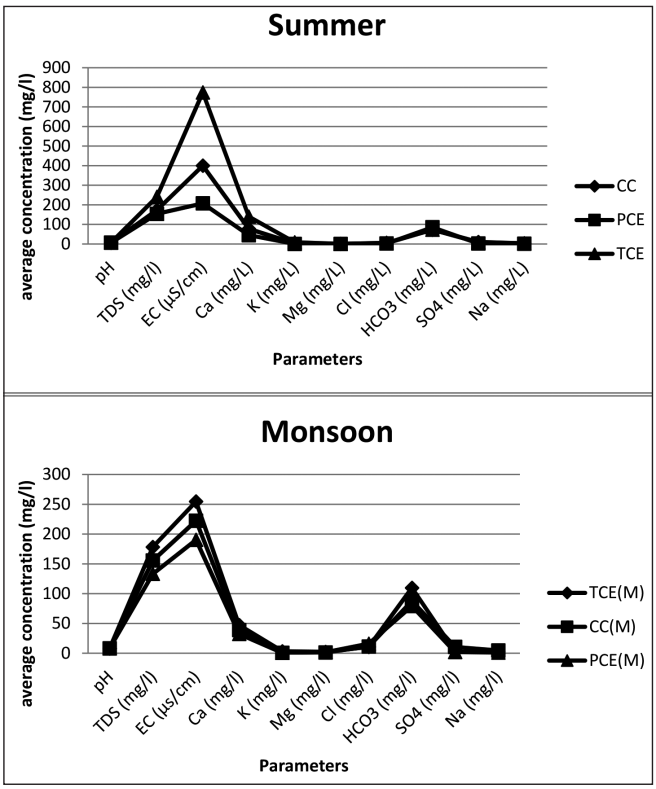

Figure 3: Average concentration of chemical parameters in three localities during summer and monsoon.

than the other cave drip waters. But the concentration of Cl^- and HCO_3^- is higher in Niah cave than the other caves irrespective of seasons. Saturation index of calcite in drip waters of Niah cave is in near-saturation state, whereas the other caves show saturation to over saturation condition. Overall this comparative study indicates that the chemical signatures of Niah cave drip waters show significant variation than the other caves.

Hydrogeochemistry of Drip Waters

The geochemical evolution of water can be understood from the Piper plot (Piper, 1953). Piper diagrams (Piper, 1953) are drawn by plotting the proportions (in equivalents) of the major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) on one triangular diagram, the proportions of the major anions (CO_3^-, HCO_3^-, Cl^-, SO_4^{-2}) on another triangular diagram, and combining the information from the two triangles on a quadrilateral. The position of this plotting indicates the relative composition of groundwater in terms of the cation–anion pairs that correspond to four vertices of the field. In the Piper plot, all the samples falling in Ca-HCO_3 facies indicate recent recharged water from the monsoonal rainfall (Figure 4). It also indicates the carbonate dissolution through water-rock interaction. Similar water facies was noted in summer season. Gibbs (1970) proposed a method for detecting the relationship between water composition and mechanism controlling their chemistry. In the Gibbs plot, all the samples fall in weathering zone indicating the chemical weathering with the dissolution of rock forming minerals as the major controlling process for the composition of drip water, which is similar to the summer season (Figure 4).

The partial pressure of CO_2 (pCO_2) in rivers is commonly out of equilibrium with the atmosphere. The log pCO_2 for each sample is determined to study its relation to recharge. The atmospheric log pCO_2 value is around –3.75 (Raymahashay, 1986). Water with high pCO_2 of around –1.5 results due to deep circulation of ground waters, with less atmospheric interaction or due to high saturation of carbonates, resulting from the interaction with the host rock of the material through which it flows (Stumm and Morgan, 1995; Lower,

Table 2: Comparison of average chemical composition of drip waters in Niah Cave with few other caves in the world (all values in mg/l, except temperature in °C and pH)

Location	*Temp*	*pH*	*TDS*	*Ca^{2+}*	*K^+*	*Mg^{2+}*	*Cl^-*	*HCO_3^-*	*SO_4^{2-}*	*Na^+*	*SIc*
Heshang Cave, Central China (*n* = 2)	18.2	7.7	233.8	66.1	0.5	41.1	0.7	193.5	19.1	1.3	0.3
Xueyu Cave, SW China (*n* = 12)	17.6	7.5	539.2	175.2	0.6	4.0	2.1	477.8	53.2	1.0	0.9
Wombeyan Caves, SE Australia (*n* = 73)	NA	7.7	NA	89.3	0.5	1.8	7.6	359.0	2.6	2.9	0.6
Guizhou Caves, China (*n* = 5)	14.8	8.1	NA	52.9	0.4	23.6	1.6	273.5	6.4	1.4	0.7
Pettyjohns Cave, NW Georgia, USA (*n* = 4)	12.8	7.7	235.3	53.8	0.5	2.3	2.2	163.3	7.4	0.7	0.4
Niah Great Cave, east Malaysia (Summer, *n* = 3)	25.3	6.8	189.2	87.3	3.9	0.3	4.3	77.3	6.8	2.4	-0.8
Niah Great Cave, east Malaysia (Monsoon, *n* = 9)	25.0	8.2	160.8	41.0	1.6	1.7	11.6	94.2	7.0	3.6	-0.1

NA – not available, *n* – number of samples, SIc – saturation index of calcite.

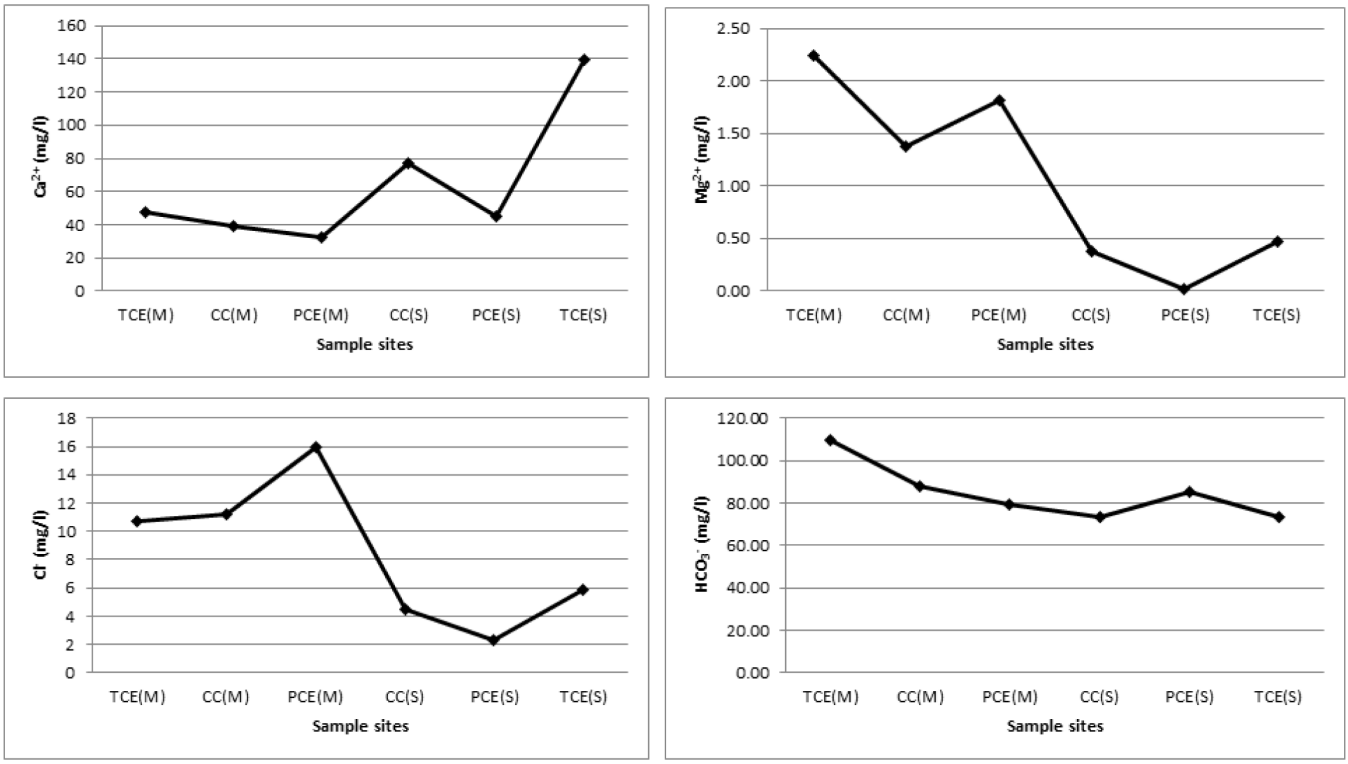

Figure 4: Seasonal trends of Ca, Mg, HCO_3 and Cl for drip waters (M – monsoon, S – summer).

1999; Chidambaram et al., 2011). In mixed water, pCO_2 tends to decrease to the atmospheric value and this causes increase in saturation, suggesting that the mixing zone is an open system (Raymahashay, 1986). The composition of freshwater is controlled by dissolution and precipitation processes and by degassing of CO_2.

Log pCO_2 value ranges from –3.57 to –2.94 with an average of –3.25 in TCE, –3.54 to –3.21 with an average of –3.39 in CC and –3.353 in PCE. Ionic strength is a measure of total concentration of ions, which emphasizes increased contribution of species with charges greater than one (Domenico and Schwartz, 1998). Ionic strength ranges from 0.003 to 0.004 in TCE, 0.003 to 0.005 in CC and 0.002 in PCE. In general, it was observed that the TCE samples show slightly higher pCO_2 and IS values compared to CC and PCE samples (Figure 5). It indicates that TCE waters have comparatively longer residence time in the cave bed rock fissures or high flushing rate of recharge water, which released more ions into the drip water through water-rock interaction due to the variations in pressure and temperature conditions.

The aqueous speciation computed with WATEQ4F program (Ball and Nordstrom, 1992) was used to define possible chemical reactions in the aquifers and to assess the state of equilibrium between water and minerals. The saturation indices and activities of constituents were calculated by using WATEQ4F program. In general, the saturation index of carbonate minerals indicates that the dolomite and magnesite are in the state of under-saturation. Further, calcite and aragonite are from under-saturation to over-saturation condition irrespective of samples (Figure 6). But, it is interesting to note that the SI of calcite in TCE and PCE drip waters are in under-saturation condition indicating the dissolution of calcite by the high flushing rate of rain water into the open cave system (Figure 7). Whereas in the CC drip waters, it ranges from near-saturation to over-saturation condition which indicate the initial flushing of recharge water and slowly percolate into the closed cave system to precipitate the calcite. The outgassing of CO_2 drives the carbonate equilibrium towards calcite precipitation. During outgassing, bicarbonate is lost through conversion to CO_2 and the pH must rise to maintain the charge balance by decrease in pCO_2 (Toran and Roman, 2006). But, outgassing occurs faster than $CaCO_3$ precipitation, which leads to oversaturation (Freeze and Cherry, 1979). Lesser HCO_3^- and pCO_2 values and increasing pH value in CC drip waters may substantiate the above statement. In summer season, all the samples were in under-saturation condition.

Factor analysis was performed to identify the most important factors contributing to the data structure and similarities between the factors. When the factor

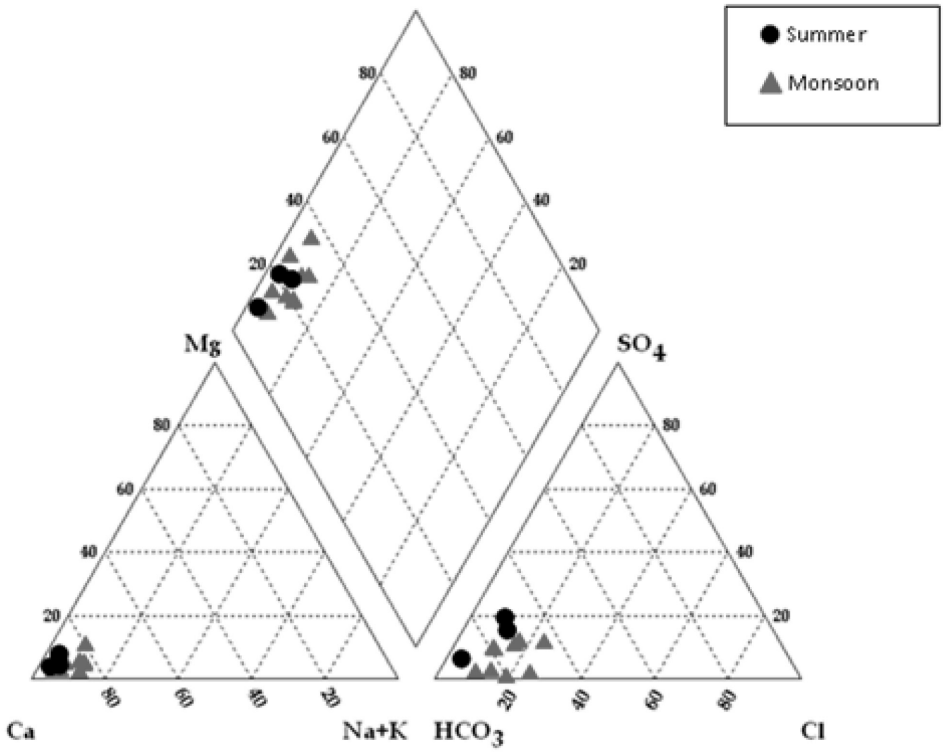

Figure 5: Piper plot for drip water samples.

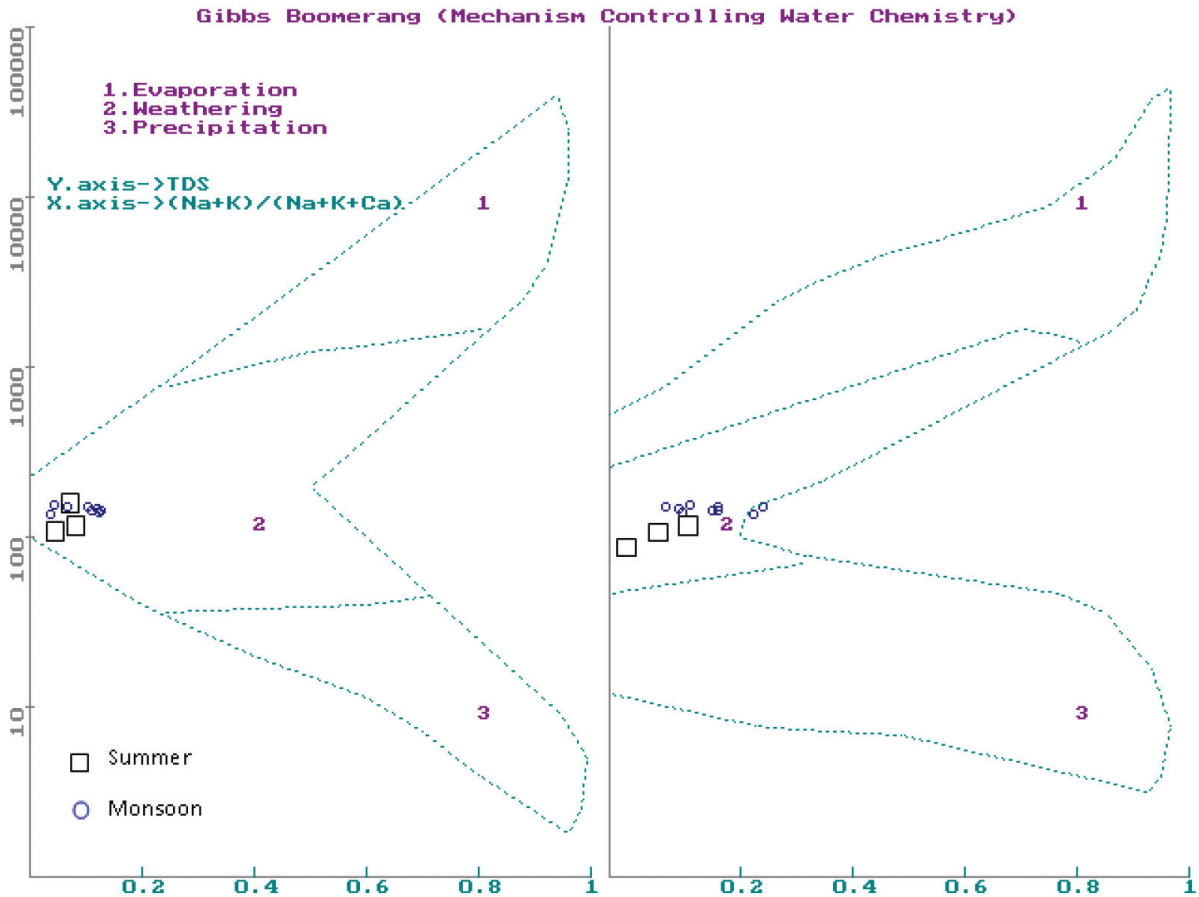

Figure 6: Gibbs plot for the drip water samples.

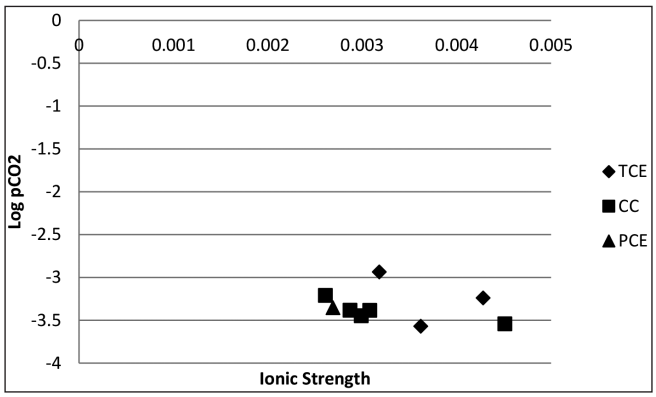

Figure 7: Relationship between log pCO_2 and ionic strength in monsoon season.

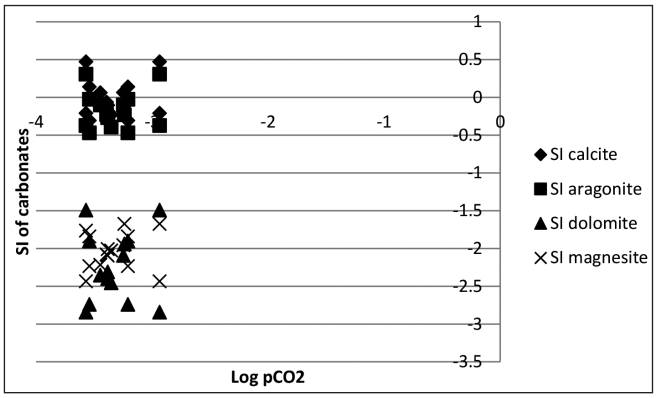

Figure 8: Relationship between log pCO_2 and SI of carbonates in monsoon season.

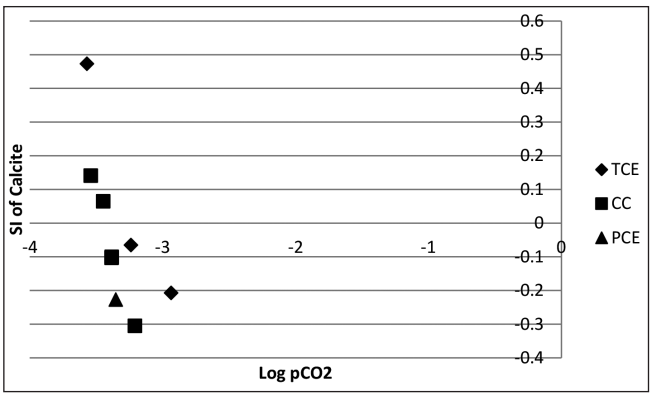

Figure 9: Relationship between log pCO_2 and SI of calcite in monsoon season.

analysis is applied to chemical data of drip water, dominant processes can be identified as common factors that are sets of variables having strong associations with one another (Ritzi et al., 1993; Prasanna et al., 2010; Vasanthavigar et al., 2010). Three most significant factors were extracted with the total variance of 94.82 (Table 2).

Factors 1 and 2 are highly loaded with EC, TDS, Ca^{2+}, HCO_3^-, Mg^{2+} and K^+. The contents of Ca^{2+}, Mg^{2+} and HCO_3^- in the drip water could be controlled by the carbonate mineral–water equilibrium (Jeong, 2001) based on the following reaction:

$$(Ca_{1-x}Mg_x)\ CO_3 + H_2O + CO_2 \rightarrow \ (1–x)\ Ca + x Mg + 2HCO_3$$

K^+ may be derived from the leaching of clay minerals coating on the surface of the host rock.

Factor 3 loaded with SO_4^{2-} and Na^+ is probably derived from the ion-exchange in soils and clastic rock units (Mayer, 1999). Factor 4 is loaded with pH and Cl^-. During water-rock interaction, two different modes can release the major elements into the solution (Grimaud et al., 1990): (1) controlled elements (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-), which quickly limit their concentration by the precipitation of a sparingly soluble mineral phase and immobilized; and (2) soluble elements, which steadily increase during the evolution of water and remain in the solution phase. Cl^- is the typical soluble element and it indicates the degree of reaction progress of the dissolution, whereas the pH of drip water is buffered by the hydrogen production and consumption reactions.

Table 3: Factor analysis for drip water samples in monsoon season

	Factors			
Parameters	*1*	*2*	*3*	*4*
pH	.396	-.414	.199	**.649**
TDS	**.989**	.094	-.065	-.008
EC	**.989**	.094	-.065	-.008
Ca	**.630**	**.614**	.019	.408
K	.152	**.916**	-.223	-.066
Mg	.061	**.943**	-.236	.151
Cl	-.123	.261	-.176	**.903**
HCO_3	**.578**	-.562	-.322	-.486
SO_4	-.167	-.205	**.944**	.119
Na	.026	-.147	**.969**	-.156
Total	2.913	2.744	2.121	1.705
% of Variance	29.129	27.437	21.205	17.051
Cumulative %	29.129	56.565	77.771	94.822

Conclusions

The hydrogeochemical characteristics of drip water in Niah Great Cave have been conclusively summarized as follows.

The total ionic concentration of drip water collected in monsoon period is less than in summer period. It indicates the high flushing rate with less residence time of recharge water into the cave system in monsoon period. pH of the drip water was in alkaline condition in monsoon period and near-acidic to neutral condition in summer period. Due to near-acidic condition, more ions have been released by water-rock interaction in the summer period. Ca-HCO_3 is the most common water type observed in both the seasons which indicates the dissolution of carbonate minerals. SI of calcite shows near-saturation to over-saturation condition in CC drip waters which indicate the precipitation of carbonate minerals due to the slow infiltration of recharge water into the closed cave system. Whereas under-saturation condition was observed in TCE and PCE drip waters indicating the dissolution of carbonate minerals due to the high flushing of recharge water. The factor analysis of chemical data reveals that Ca^{2+}, Mg^{2+} and HCO_3^- were highly loaded in Factors 1 and 2 which indicate the dissolution of carbonate minerals by water-rock interaction as the major controlling process for the drip water geochemistry. The influence of monsoon climate drives the precipitation and CO_2 concentration, which has changed the intensity of water-rock interaction and results in the seasonal variation of drip waters geochemistry in Niah Great Cave.

Acknowledgements

The authors thank the Curtin University Sarawak, for the financial support through CSCRS Project (CSCRS4020). The authors are also thankful to the Controller of national parks and nature reserves, Sarawak Forest Department, for granting permission to conduct research in Niah Great Cave. Pengarah, Jabatan Meterologi Malaysia, Cawangan Sarawak is gratefully acknowledged for providing rainfall data from Niah forest office. Special thanks to Dr. Dominique Dodge-Wan (Curtin University Sarawak) and Mr. S. Devaraj (Annamalai University, India), for their help in sampling and data plotting. The authors are also grateful to the anonymous referees for their constructive comments and suggestions, which led to significant improvements to the manuscript.

References

APHA (1995). Standard methods for the examination of water and waste water, 19th edn. APHA, Washington DC, USA.

Atkinson, T.C., 1977. Carbon dioxide in the atmosphere of the unsaturated zone: An important control of groundwater hardness in limestones. *Journal of Hydrology*, **35:** 111-123.

Baker, A., Genty, D. and 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. and Fairchild, I.J., 2006. Spatial variability in cave drip water hydrochemistry: Implications for stalagmite paleoclimate records. *Chemical Geology*, **235(3-4):** 390-404.

Ball, J.W. and Nordstrom, D.K., 1992. User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of minor, trace and redox elements in natural waters. U.S. Geol. Surv., Open File Rep. 91-183, 189.

Chidambaram, S., Prasanna, M.V., Karmegam, U., Singaraja, C., Pethaperumal, S., Manivannan, R., Anandhan, P. and Tirumalesh, 2011. Significance of pCO^2 values in determining carbonate chemistry in groundwater of Pondicherry region, India. *Front Earth Sci*, **5(2):**197-206.

Domenico, P.A. and Schwartz, W., 1998. Physical and chemical hydrogeology, 2nd edn. Wiley, New York.

Dreybrodt, W., 1988. Processes in karst systems. Springer-Verlag.

Ducci, D., Masi, G. and Priscoli, G., 2008. Contamination risk of the Alburni Karst System (Southern Italy). *Eng Geol*, **99:** 109-120.

Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spotl, C., Mattey, D., McDermott, F. and E.I.M.F., 2006. Modification and preservation of environmental signals in speleothems. *Earth Science Reviews*, **75:** 105-153.

Fairchild, I.J. and McMillan, E.A., 2007. Speleothems as indicators of wet and dry periods. *International Journal of Speleology*, **36(2):** 69-74.

Ford, D.C. and Williams, P.W., 2007. Karst hydrogeology and geomorphology. John Wiley and Sons, Chichester.

Freeze, A.R. and Cherry, J.A., 1979. Groundwater. Prentice-Hall Inc., Englewood Cliffs.

Gibbs, R.J., 1970. Mechanisms controlling world's water chemistry. *Science*, **170:** 1088-1090.

Hagedorn, B. and Cartwright, I., 2009. Climatic and lithologic controls on the temporal and spatial variability of CO_2 consumption via chemical weathering: An example from the Australian Victorian Alps. *Chem Geol*, **260:** 234-253.

Han, G. and Liu, C., 2004. Water geochemistry controlled by carbonate dissolution: A study of the river waters draining karst-dominated terrain, Guizhou Province, China. *Chem Geol*, **1:** 1-21.

Hem, J.D., 1985. Study and interpretation of the chemical characteristics of natural water. U S Geol Surv Water Supply Pap, **2254:** 117-120.

Hunt, C.O. and Rushworth, G., 2005a. Cultivation and human impact at 6000 calyr BP in tropical lowland forest at Niah, Sarawak, Malaysian Borneo. *Quatern Res*, **64:** 460-468.

Hunt, C.O. and Rushworth, G., 2005b. Airfall sedimentation and pollen taphonomy in the West Mouth of the Great Cave, Niah. *J. Archaeol Sci*, **32:** 465-473.

Hutchinson, C.S., 2005. Geology of North-West Borneo: Sarawak, Brunei and Sabah. Elsevier, Amsterdam.

Jeong, Chan-Ho, 2001. Mineral-water interaction and hydrogeochemistry in the Samkwang mine area, Korea. *Geochemical Journal*, **35:** 1-12.

Johnson, K.R., Hu, C., Belshaw, N.S. and Henderson, G.M., 2006. Seasonal trace element and stable isotope variations in a Chinese spelothem: The potential for high-resolution paleomonsoon reconstruction. *Earth and Planetary Science Letters*, **244(1-2):** 394-407.

Kaufmann, G., 2009. Modelling karst geomorphology on different time scales. *Geomorphology*, **106:** 62-77.

Liu, Z., Dreybrodt, W. and Wang, H., 2008. A possible important CO_2 sink by the global water cycle. *Chin Sci Bull*, **3:** 402-407.

Lower, S., 1999. Carbonate equilibria in natural waters. *In:* Digital Textbook Chapters. http://www.chem1.com/acad/pdf/c3carb.pdf.

Mayer, J., 1999. Spatial and temporal variation of groundwater chemistry in Pettyjohns cave, northwest Georgia, USA. *J. CaveKarst Stud*, **61(3):** 131-138.

McDonald, J., Drysdale, R. and Hill, D., 2004. The 2002-2003 El Nino recorded in Australian cave drip waters: Implications for reconstructing rainfall histories using stalagmites. *Geophysical Research Letters*, **31** (L22202). Doi 10.1029/2004GL020859

Mocochain, L., Audra, P., Clauzon, G. et al., 2009. The effect of river dynamics induced by the Messinian Salinity Crisis on karst landscape and caves: Example of the Lower Ardèche river (mid Rhone valley). *Geomorphology*, **106:** 46-61.

Piper, A.M., 1953. A graphic procedure I the geo-chemical interpretation of water analysis. USGS Groundwater Note no, 12.

Prasanna, M.V., Chidambaram, S. and Srinivasamoorthy, K., 2010. Statistical analysis of the hydrogeochemical evolution of groundwater in hard and sedimentary aquifers system of Gadilam river basin, South India. *Journal of King Saud University (Science)*, **22:** 133-145.

Prasanna, M.V., Nagarajan, R., Chidambaram, S., Manikandan, S. and Elayaraja, A., 2014. Drip water geochemistry of Niah Great Cave, NW Borneo, Malaysia: A base line study. *Carbonates Evaporites*, **29:** 41-54.

Raymahashay, B.C., 1986. Geochemistry of bicarbonate in river water. *J Geol Soc India*, **27:** 114-118.

Ritzi, R.W., Wright, S.L., Mann, B. and Chen, M., 1993. Analysis of temporal variability in hydrogeochemical data used for multivariate analyses. *Groundwater*, **31:** 221-229.

Spotl, C., Fairchild, I.J. and Tooth, A.F., 2005. Cave air control on dripwater geochemistry, Obir Caves (Austria): Implications for speleothem deposition in dynamically ventilated caves. *Geochimicaet Cosmochimica Acta*, **69(10):** 2451-2468.

Stanley, S.M., Ries, J.B. and Hardie, L.A., 2002. Low-magnesium calcite produced by coralline algae in seawater of Late Cretaceous composition. *PNAS*, **99(24):** 15323-15326.

Stumm, Werner and Morgan, James. 1995. Aquatic chemistry 3rd, Ed. Wiley.

Tooth, A.F. and Fairchild, I.J., 2003. Soil and karst aquifer hydrological controls on the geochemical evolution of spelethem forming drip waters, Crag cave, southwest Ireland. *Journal of Hydrology*, **273:** 51-68.

Toran, L. and Roman, E., 2006. CO_2 outgassing in a combined fracture and conduit karst aquifer near Lititz Spring, Pennsylvania. Geol Soc Am Spec Pap, **404:** 275-282.

Vasanthavigar, M., Srinivasamoorthy, K. and Prasanna, M.V., 2013. Identification of groundwater contamination zones and its sources by using multivariate statistical approach in Thirumanimuthar sub-basin, Tamil Nadu, India. *Environmental Earth Sciences*, **68:** 1783-1795.

White, W.B., 1988. Geomorphology and hydrology of karst terrains. Oxford University Press, New York.

Xiao, H. and Weng, Q., 2007. The impact of land use and land cover changes on land surface temperature in a karst area of China. *J. of Env. Management*, **95(1):** 245-257.

Yoshimura, K., Nakao, S. and Noto, M., 2001. Geochemical and stable isotope studies on natural water in the Taroko Gorge karst area, Taiwan: Chemical weathering of carbonate rocks by deep source CO_2 and sulfuric acid. *Chem Geol*, **3:** 415-430.

Yuan, D., 1997. Sensitivity of karst process to environmental change along the PEP II transect. *Quatern Int*, **35:** 105-113.

Yuan, D., Liu, Z., Lin, Y., Shen, J., He, S., Xu, S., Yang, L., Li, B., Qing, J., Cai, W., Cao, J., Zhang, M., Jiang, Z. and Zhao, J., 2002. Karst dynamic system of China. Geological Publish House, Beijing. (In Chinese)