

CHAPTER 1: INTRODUCTION

1.1 Introduction

In recent years there has been a growing interest in understanding karst system (Fairchild et al., 2000, Baker et al., 2000, Tooth and Fairchild, 2003, Baldini et al., 2006, McDonald et al., 2007 and Karmann et al., 2007). Most of the detail study concentrates on the hydrochemistry of drip water. Predominantly, the study has been carried out in temperate region such as Australia, United Kingdom, and Europe. The study comes up with new idea and assumption leading to a more comprehensive characterization of the spatial and temporal hydrogeochemistry of the karst water. On the other hand, there are variance in the study areas, geology and climate that might complicate the interpretation. In particular, how hydrogeochemistry acts in tropical region caves, especially Peninsular Malaysia is still an open question, since there is very little study have been done.

The motivation of this study is to proof the significant relationship between drip water and climatic parameters. Therefore, this study shows new results of physical and chemical properties of drip water in selected caves in Peninsular Malaysia. This preliminary study is a great relevance study for interpreting the characteristic of drip water hydrogeochemistry.

1.2 Objectives of the study

- 1.2.1: To determine the physical and chemical characteristic of drip water.
- 1.2.2: To study the hydrogeochemistry of drip water including the water rock interaction process in karst system.
- 1.2.3: To develop a conceptual model for the karst system.

1.3 Study Area

Study areas are located in scattered limestone caves in Peninsular Malaysia (Figure 1.1). The study carried out at Batu Caves, Selangor and Gunung Tempurung, Perak. In North of Peninsular Malaysia, the study area is situated at Gua Kelam, Perlis and Gua Berlian, Kedah. The study is also conducted at Gunung Senyum and Gunung Jebak Puyuh located in the Eastern part of Peninsular Malaysia.. (Details description can be found in Chapter 3)

1.3 The Distribution and Description of Malaysian Karst

Southeast Asia consists some of the widespread karst region in the world. The karst landscapes are widely distributed in Malaysia, Thailand, Brunei, Indonesia, Cambodia, Vietnam, Papua New Guinea and Philippines. The moist environment of tropical and subtropical areas of South East Asia favor diverse and striking karst landscapes (Gillieson, 2005).

The surface limestone in the Peninsular Malaysia covers approximately about 0.3% (Figure 1.1) of the country's 330,000-sq kilometer total landmass (Muhammad, 2003 and Zulkifli, 2003). Generally, Malaysian limestone formation lies on the belt along the axis of Peninsular Malaysia and in northern Sarawak (Gillieson, 2005). Instead, most of spectacle karst lands in Peninsular Malaysia are widely distributed in the northern half of west part comprises Perlis, Kedah, Perak, and Selangor (Hutchison, 1968, Muhammad, 2003, Zulkifli, 2003, and Gillieson, 2005). Karst landscapes can also be found in the eastern part of Peninsular Malaysia which covers Pahang, Kelantan and Terengganu.

Setul Limestone terrain that scattered in the North of Peninsular Malaysia comprises Langkawi Island, east of Kedah and Perlis near the Thai border (Gillieson, 2005). Crowther (1982) explained that Setul Limestone is characterized by high proportions of argillaceous and siliceous impurity and has been dated to be Ordovician to Silurian (Hutchison, 1968). Kuala Lumpur Limestone is dated Middle to Upper Silurian and covers Kuala Lumpur and Selangor. Kinta Valley, Perak is overlain by Kinta Valley Limestone. In addition, the most spectacle karst morphology exhibits in the centre of Peninsular Malaysia are Kota Gelanggi Complex, Gunung Senyum Complex and Gunung Jebak Puyuh Complex in Pahang (Zulkifli, 2003). Karst topography can also be found at Bukit Biwah and Bukit Taat, Terengganu which are located at eastern part of Peninsular Malaysia (Mohamed et. al., 2001).

The tropical limestone massif illustrates distinctive geomorphology formations and structures, forms diverse karst topography and overlain by alluvium. Most of massif limestone in Peninsular Malaysia exhibits as a *Fenglin* and *Fengcong* (Gillieson, 2005) styles of tropical karst. Gillieson (2005) explained the best terminology for broad-scale of

karst geomorphology which is *Fenglin*, characterized by a forest of limestone tower standing above a comparatively flat and often alleviated plain. On the other hand, *Fengcong* is a peak-cluster depression which has a large number of closed polygonal depressions united on a rock base and elevated above the surrounding terrain. The wide range of karst geomorphology depends on local details of structure and lithology (Gillieson, 2005, Crowther, 1982 and Hutchison, 1968).

Extensive studies by the Institute for Environment and Development (LESTARI) determined that karst landscape is very unique and have a high value in terms of scientific and aesthetic aspects (Komoo et al., 2001). In addition, archeological excavation has been done around Pahang, Terengganu and Kelantan discovers that the valuable artifacts widely distributes in limestone caves which is proved of an ancient culture (Zulkifli, 2003). For example, small cutting and scraping knife-type tools made from pebbles were found at Tok Long Cave in Gunung Senyum. The study concluded that limestone caves were comprehensively occupied as rock shelters by early Hoabinhian, Neolithic and Bronze Age hunter and gatherer communities.

1.4 Literature review

Recent utilization of drip water has proven success reconstruction of paleoclimate records (Genty et al, (1998), Baldini et al., (2006) and McDonald et al., (2007). Drip water defined as vadose percolation flow paths truncated by a cave and integral as a part of the aquifer's hydrological system (Baldini et al., 2006). Drip water studies have received special attention because isotopic and chemical compositions of speleothems, especially

stalagmites records temporal changes reflected by environmental condition. Furthermore, cave environment have an advantage as it experienced small rate of erosion due to its enclosed environment (Ford and William, 1989).

Existing literature on limestone hydrology and hydrogeochemistry is mostly focusing at the spatial and temporal variability of drip water. Previous study of karst hydrology provides an understanding of the factor that controls the drip discharge. Tooth et al., (2003), Baldini et al., (2006), McDonald et al., (2007) and Fernandez-Cortes et al., (2008) produced a flow classification scheme based on variations in rate and maximum discharge, from which they developed basic hydrological changes in flow rate with recharge in karst system.

The infiltration process acts differently according to the hydrological properties at each site of drip water (Genty et al., 1998, Baldini et al., 2006, McDonald et al., 2007 and Fernandez-Cortes et al., 2008). The study of variation in drip rates with antecedent rainfall determined that the hydrological behavior at drip sites varies accordingly to the overall volume of water input in karst system Tooth et al., (2003), Fairchild et al., (2006), Baldini et al., (2006), McDonald et al., (2007) and Fernandez-Cortes et al., (2008). In addition, McDonald et al., (2007) and Baldini et al., (2006) explained that the behavior of drip water is varies according to the delivery potential and mechanism at each drip sites. The study determined that the drip water can be classified into: seasonal flow, seepages flow, percolation flow, vadose flow, subcutaneous flow and shaft flow.

Genty et al., (1998) and Baker et al., (2000) claimed that the increased of conductivity as a result of the increment of water residence time in reservoir. This

phenomenon implies that the low water input during dry period, trigger a small amount of water accumulation in reservoir and the hydraulic pressures become low coincidentally with a slow water infiltration in pores and microfissures in the system.

Extensive study of drip water hydrogeochemistry revealed that the significant factors acts in karst system such as residence times of percolation water, prior calcite precipitation at individual drip sites, volume of water input, flow routes taken at each drip sites and the host rock composition (Fairchild et al., 2000, Tooth et al., 2003, Baldini et al., 2006 and Karmann et al., 2007). Generally, the chemistry contents of drip waters consist of Ca and HCO_3 as dominant elements. Whilst, other chemistry contents such as NO_3 , Cl, SO_4 must be significant related to the source rock and human activities either outside or inside of the caves (Tooth et al., 2003).

Detail discussion mostly focuses on the variability of Ca and Mg which rations allows to differentiate a rock water process in karst system such as prior calcite precipitation, dissolution and dilution processes (McDonald et al., 2007, Fairchild et al., 2006, Karmann et al., 2007, Baldini et al., 2006 and Tooth et al., 2003). The studies determine that the Calcite Saturation Index ($SI_{calcite}$) is increased during summer and decreased during winter. This is due to low water storage in karst system during low rainfall trigger a proportion of ventilated air pocket reservoir and derived degassing of CO_2 from solution, causing calcite precipitation along flow routes. Besides, a longer mean residence times of drip water is favoring the increment of $SI_{calcite}$ and enrichment in Mg. Therefore, the increases of $SI_{calcite}$ involve the increase of Mg/Ca ratios and vice versa.

1.6 METHODOLOGY

1.6.1 Desk study

Literature review of previous works has been carried out to gain a better knowledge of geology, geochemistry and hydrology of the study area. The literature review was completed by referring previous study from articles, journals, published and unpublished theses. The rainfall data was obtained from Meteorological Department of Malaysia (MET). The rainfall distribution in Peninsular Malaysia was analyzed and interpreted.

1.6.2 Fieldwork

Monitoring was performed on a fortnightly time scale at Villa Cave and Dark Cave in October 2007-October 2008 and March 2008 – May 2008, respectively. Monthly sampling was conducted at Gua Tempurung in February 2008 – March 2009. Only few sampling trip were performed at Gua Straw (Gunung Jebak Puyuh), Gua Angin (Gunung Senyum), Gua Berlian (Kaki Bukit), Gua Kelam and Gua Wang Burma (Kaki Bukit) due to distance and accessibility to certain caves. Meteoric water also has been collected in several sites such as Ipoh and Kuala Lumpur.

In order to fulfill the objectives, sites were chosen from different localities along the cave passages. The sampling points were selected from a wide range of speleothems which consists of stalactites, fracture opening, stagnant water, river and spring (Table 1.1). This strategy was employed to gain better understanding of hydrogeochemistry of drip water.

Table 1.1 : List of study areas.

Location		Sample types
Selangor	Villa Cave, Batu Caves	Drip water
	Dark Cave, Batu Caves	Drip water
Perak	Gua Tempurung	Drip water, spring, pond and river
Pahang	Gua Angin, Gunung Senyum	Drip water
	Gua Straw, Jebak Puyuh	Drip water
	Gua Haluan Kapal	Drip water
Kedah	Gua Berlian	Drip water
	Gua Layang-layang	Drip water
Perlis	Gua Kelam	Drip water

1.6.3 Sampling Method

All samples were collected using acid-washed low density polyethylene (LDPE) bottles. The in-situ parameter measured consists of conductivity, Total Dissolved Solid (TDS), Dissolved Oxygen (DO), pH and temperature. The parameters were measured in all the caves except in Gua Tempurung, Gunung Tempurung and Gua Straw, Gunung Jebak Puyuh due to logistic of carrying equipment into the cave. The measurements were not performed on all samples because of the small sample sizes especially in drip water from Gua Straw, Gua Kelam and Gua Wang Burma. Drip rates were measured using bucket method as how much time taken for the drip water to accumulate in 10 ml cylinder (McDonald et al., 2007).

Upon collection, the samples were divided into two aliquots. In aliquot, the samples were acidified using distilled HNO₃ (70%) to pH 2-4 to redissolve any precipitated calcite, then filtered through 0.45 using a NalgeneTM pump filter. Acidified samples were analyses for cation species by Inductively Coupled Plasma Optical Emission Spectrometers (Perkin-Elmer). The second un-acidified aliquot was refrigerated prior to analyses for anion species and alkalinity by Ion Chromatography and Auto-titrator (Methrom). All laboratory analyses were carried out at Department of Geology, University of Malaya.

A care was taken at each step of the analysis to ensure consistent results:

- a) Avoid cross-contamination.
- b) Proper calibration of measurement equipment.
- c) All samples were collected in duplicate except for insufficient samples due to slow drip.

1.6.4 Data Analyses and Presentation

Collectively, all the data were interpreted and presented using statistic analysis and graphical method. All the data analyses were conducted using Microsoft Office and AQUACHEM software. AQUACHEM is a complete software with several programs such as PHREEQC and WATEFAL that provide selection of analysis tools, calculation and graph for interpreting water quality data based on physical and chemical parameter. AQUACHEM also comprises with multi-component plots such as PIPER diagram and Stiff diagram. Source rock deduction was evaluated by PHREEQC program to emphasize the hydrogeochemistry of the water based on various element ratios such as $(\text{Na}+\text{K}-\text{Cl})/(\text{Na}+\text{K}-\text{Cl}+\text{Ca})$, $\text{Mg}/(\text{Ca}+\text{Mg})$ and $\text{Ca}/(\text{Ca}+\text{SO}_4)$. The formula used by PHREEQC to calculate the SI_{calcite} is shown below:

$$\text{a) } SI_{\text{calcite}} = \frac{\log (\text{Ca}^{2+})(\text{HCO}_3^-)K_2}{(\text{H}^+)(K_c)}$$

1.7 Constraints and Limitations

Several constraints and limitations were experienced during the process of water collection and laboratory analyses, which might have influenced the accuracy of the results obtained.

- a) Most of the accessible caves are open to public, therefore it is impossible for continuing monitoring using the portable auto-sampler due to security issues.
- b) Few samples were collected overnight to allow sufficient volume to accumulate at slow drip sites in Gua Tempurung.

c) Not all samples were managed to be collected during each sampling times. It depended on the circumstances. For example, during raining season, the western part Gua Tempurung is flooded and not suitable to be explored. Meanwhile, Villa Cave was under construction of reptile museum starting the end of December 2007 until February 2008. The sampling sites have been disturbed and only two sites were left suitable for continuous sampling.