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Geochemistry, Evolution and Mixing Estimation of Groundwater for Identifying Zones Affecting the Stability of Rock Slopes

A dissertation submitted in partial fulfillment of the
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Engineering

by

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ABSTRACT

Groundwater is a really crucial factor in rock slope issues of limestone quarries. After a limestone deposit is mined out, a huge final slope is left in the mountainous area. This leads to slope instability as a major problem. This instability frequently suffers from the effects of groundwater. Although the effects of groundwater level and flow on the mechanical properties of limestone itself have been adequately investigated in previous researches, monitoring and assessment of geochemical properties and geochemical processes of groundwater for rock slopes are rarely reported. Therefore, this dissertation focused on the geochemistry, evolution and mixing estimation of groundwater of an open-pit limestone quarry in Japan for identifying zones affecting the stability of rock slopes. In addition, tritium concentrations of groundwater were also analyzed for groundwater age estimation and extensive comprehension. The followings are the summaries of each chapter in the dissertation.

In Chapter 1, the general introduction of limestone, groundwater managements, groundwater chemistry and groundwater effects on rock slopes are described. The statement of the problem and objectives of the study are highlighted to understand the key points of context and structure of the entire research.

Groundwater flow and its geochemical evolution in mines are important not only in the study of contaminant migration but also in the effective planning of excavation. The effects of groundwater on the stability of rock slopes and other mine constructions, especially in limestone quarries, are crucial because calcite, the major mineral component of limestone, is moderately soluble in water. In Chapter 2, evolution of groundwater in the limestone quarry located in Chichibu city of Saitama prefecture, Japan was monitored to understand the geochemical processes occurring within the rock strata of the quarry and changes in chemistry of groundwater, which suggests zones of deformations that may affect the stability of rock slopes. There are three distinct geological formations in the quarry: limestone layer (covering), interbedded layer of limestone and slaty greenstone, and slaty greenstone layer (basement). Although the hydrochemical facies of all groundwater samples were Ca-HCO₃ type water, changes in the geochemical properties of groundwater from the three geological formations were observed. In particular, significant changes in the chemical properties of several groundwater samples along the interbedded layer were observed, which may be attributed to the mixing of groundwater from the limestone and slaty greenstone layers. On the rainy day, the concentrations of Ca²⁺ and HCO₃⁻ in groundwater fluctuated notably, and the groundwater flowing along the interbedded layer was likely to be dominated by groundwater from the limestone layer. These suggest that groundwater along the interbedded layer may affect the stability of rock slopes.

Water-rock interaction and groundwater mixing phenomena are important in understanding hydrogeological systems and the stability of rock slopes especially in limestone quarries consisting largely of moderately water-soluble minerals like calcite. In Chapter 3, water-rock interaction in the open-pit limestone quarry was evaluated using PHREEQC, while hierarchical cluster analysis (HCA) and principal component analysis (PCA) were used to classify and identify water sources responsible for possible groundwater mixing within rock layers. The results showed that the water-rock interaction within the quarry was distinguished by individual layers, all of which were geochemically involved in calcite dissolution. The changes in Ca²⁺ and HCO₃⁻ concentrations of several groundwater samples along the interbedded layer found to result from mixing groundwater from the limestone layer and that from slaty greenstone layer. Based on the HCA and PCA results, groundwater samples were classified into three types depending on their origin: (1) groundwater from the limestone layer

(L_O), (2) mixed groundwater flowing along the interbedded layer (*e.g.*, groundwater samples L-7, L-11, S-3 and S-4), and (3) groundwater originating from the slaty greenstone layer (S_O). These results suggest the necessity of continuous monitoring of groundwater.

Estimation of groundwater mixing ratios and tritium analysis are the crucial tasks in groundwater management especially for identifying sensitive zones affecting rock slopes, while tritium, a radioactive isotope, is effective in predicting groundwater age. In Chapter 4, Geochemist's Workbench was applied to estimate the mixing fractions to clarify sensitive zones that could affect rock slope stability. The mixing fractions of 41% L_O :59% S_O , 64% L_O :36% S_O , 43% L_O :57% S_O and 25% L_O :75% S_O on the normal days corresponded to groundwaters L-7, L-11, S-3 and S-4, respectively, while the mixing fractions of groundwaters L-7 and L-11 (61% L_O :39% S_O and 93% L_O :7% S_O , respectively) on rainy days became the majority of groundwater originating from the limestone layer. The tritium concentration of groundwater sample L-7 was lower than those of L-2 and LP-10 but higher than that of S-2, which explained the mixing phenomenon along the interbedded layer. All groundwater was found as modern water and the age of groundwater in the limestone layer ranged from 11~14 years, whereas that in the interbedded layer was 15 years and that in the slaty greenstone layer was older than 17 years. Regarding overall evaluation for rock slopes, the groundwater along the interbedded layer has significantly affected the stability of rock slopes by enlarging multi-breaking zones in the layer through calcite dissolution and inducing high water pressure, tension cracks and potential sliding plane along this layer, particularly during intense rainfall events.

Chapter 5 describes the overall conclusions and the suggestions for future works to develop the related studies. The geochemical survey of groundwater should be paid attention to the study of rock slope issues. Mass balance of calcite including estimation of limestone dissolution rate in the multi-breaking zones or fractures along the interbedded layer would further appear to be significant for rock slope stability. Further tritium analysis is required and ^3H - ^3He analysis method should be conducted to obtain more precise groundwater ages.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Limestone overview

1.1.1 Definition of limestone

Limestone is a common sedimentary rock composed primarily of calcite (CaCO_3), defined by Encyclopedia and is extensively used as a building material and in the making of cement, and yields lime when burned (Merriam-Webster Dictionary). On the other hand, according to Oates (1998), limestone is a naturally occurring rock consisting principally of the carbonates of calcium and magnesium, in which the ratio of CaCO_3 to MgCO_3 by weight is not less than 1.2 to 1.0.

To clearly understand the important phenomena occurring in the hydrogeological and hydrogeochemical system of an open-pit limestone quarry, this chapter discusses the background of limestone and existing groundwater in the quarry, leading to the main issues and overall objectives of this entire research.

1.1.2 Formation of limestone

The chemical components of calcium carbonate, dissolved calcium ions and carbon dioxide, are widely distributed. Calcium (Ca) is the fifth most common element in the earth's crust (after oxygen, silicon, aluminum and iron) and it is extracted from early igneous rocks by the combined effects of erosion by weathering and corrosion by acidic gases (oxides of sulfur, oxides of nitrogen and carbon dioxide dissolved in rain water). Carbon dioxide (CO_2) makes up about 0.03 % by volume of the earth's atmosphere and is dissolved in both fresh and sea water. Combination of dissolved calcium ions and CO_2 resulted in the sedimentary deposition of CaCO_3 , which is subsequently converted into limestone rock. Early limestones are believed to have been deposited as precipitates of CaCO_3 and/or as a result of the biochemical activity of very simple organisms such as bacteria (Oates, 1998). However, based on Encyclopedia limestone is a naturally occurring mineral that forms either by direct crystallization from water (usually seawater) or by accumulation of coral and shell fragments. In the first case, it carries a record of the chemical composition of seawater and it provides evidence of how that composition has changed with time. In the second case, limestone provides a record of the evolution of many important fossils. Limestone constitutes approximately 10 percent of the sedimentary rocks exposed on the earth's surface. Limestone usually forms in shallow water less than 20 m (70 ft) deep and thus also provides important geological information on the variation in sea level in the past. Limestone is frequently riddled with caves.

Many limestones are remarkably pure, with less than 5 % of non-carbonate impurities. Limestone is found in many forms and is classified in terms of its origin, chemical composition, structure, and geological formation. Because of its high Ca content, limestone is usually light in color, although many variations exist. Commercially, the term limestone includes dolomite, dolomitic limestone, oolitic limestone, and travertine (Dolley, 2007), a porous calcitic rock that is commonly formed near hot springs.

1.1.3 Limestone quarrying operation

Extraction, more commonly referred to as quarrying (a type of open pit mining), consists of removing blocks or pieces of stone from an identified and unearthed geologic deposit. Differences in quarrying techniques stem from variations in the physical properties of the deposit itself (such as density, fracturing/bedding planes, and depth), financial considerations, and the site owner's preference (Jalil *et al.*, 2014). Nevertheless, the process is relatively simple: locate or create (minimal) breaks in the stone, remove the stone using heavy machinery, secure the stone on a vehicle for transport, and move the material to storage (University of Tennessee, 2008). A flow diagram of typical quarrying operations is shown in Figure 1.1.

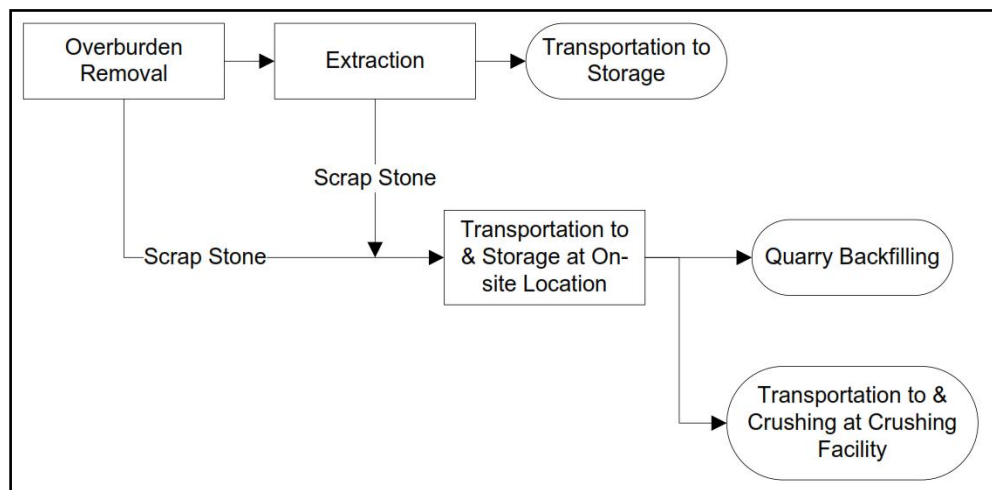


Figure 1.1 Process flow diagram for limestone quarrying operations (University of Tennessee, 2008)

As shown in Figure 1.1, the first step in quarrying is to gain access to the limestone deposit. This is achieved by removing the layer of earth, vegetation and rock unsuitable for product, collectively referred to as overburden with heavy equipment that is sometimes coupled with small explosive charges. The overburden is then transferred to onsite storage for potential use in later reclamation of the site. After the face of the limestone is exposed, the stone is removed from the quarry in benches, usually 8 to 12 feet square extending 20 feet or more using a variety of techniques suitable to the geology and characteristics of the limestone deposit. Quarrying operations typically include drilling holes along the perimeter of the bench followed by cutting the stone out of the deposit using saws equipped with diamond wire, or by splitting the stone using hydraulic splitters. If bedding planes are visible, forklifts can be used to pry up the blocks. Once the bench is cut or split loose from the deposit, heavy equipment is used to lift the limestone bench and transfer it to an inspection area for grading, temporary storage, occasional preprocessing into slabs, and eventual shipment from the site. Limestone of insufficient quality or size for current demand is stored on-site for future use, crushed for use in paving and construction applications, or stored for future site reclamation activities.

In Japan, there are many limestone mines operated by the open pit method, although no metal mine is operated by this method. In many cases, these limestone deposits are located in mountainous terrains. Therefore, mining operations can be somewhat different from the typical open pit method adopted in other countries, such as North America and Australia (Yamaguchi and Shimotani, 1986).

1.1.4 Limestone processing operation

Processing operations include much more variation than extraction. Nevertheless, the general procedures begin with initial cutting, followed by application of a finish, and conclude with a second cutting or shaping step. Due to the array of stone products, the second and/or third steps may be eliminated, specifically when the product will have a “natural” appearance. The fabrication process is depicted in Figure 1.2 (University of Tennessee, 2008).

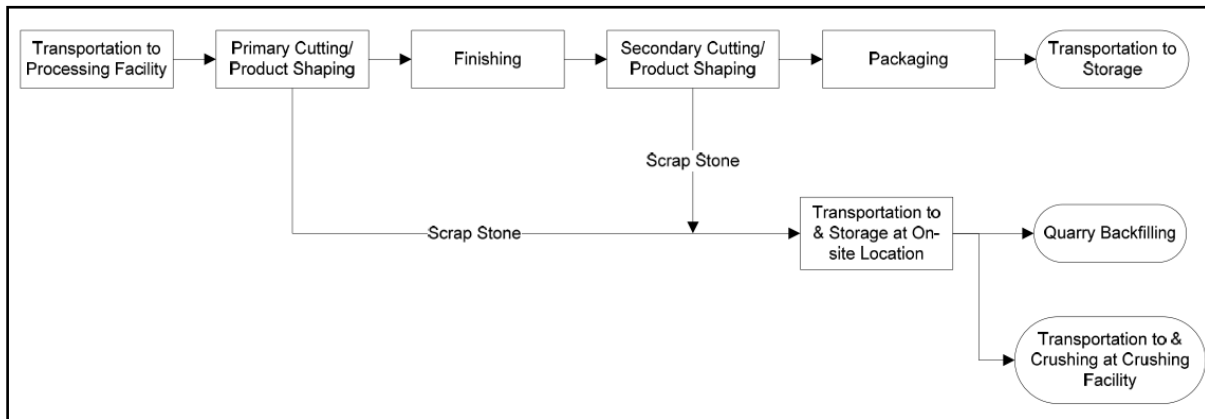


Figure 1.2 Process flow diagram for limestone processing operations (University of Tennessee, 2008)

Processing commences with transportation of the (raw) stone from the quarry to the processing facility. It should be noted that this step may consist of multiple transportation steps; prior to reaching the doors of the facility, the stone may be transferred to a number of vendors or distributed locations worldwide. Additionally, some limestone (blocks) may have been cut into slabs before reaching the main fabrication plant. These are most commonly sliced to a thickness of 3/4 in (2 cm), 1¼ in (3 cm), or more in lengths of approximately 10-12 ft and widths around 3-5 ft. The route that the stone takes through the plant therefore depends on its physical state upon arrival, as well as the product to be produced (University of Tennessee, 2008).

The first step of the process is a primary cutting or shaping of the material. This is typically accomplished for limestone using a circular blade saw, diamond wire saw, or a splitter. When operating a circular or diamond wire saw, a continuous stream of water over the saw is required in order to dissipate heat generated by the process; sufficiently elevated temperature can cause machine and material damage. Natural-faced products, such as veneer or flooring, may be completed with this step, while other products require a finishing application, secondary cutting, or both.

Limestone is often produced with a natural surface, but finishes can be applied. In such cases, often a polished or honed finishing is given to limestone products, but a variety of other finishes are also common. Polishing and honing are manually and/or mechanically accomplished through the use of polishing pads or bricks.

A secondary shaping step may be necessary if the product includes any features or custom size or shape. For this procedure, a circular blade saw is frequently implemented for limestone, but a variety of hand tools are also common. Cooling water is again necessary for large circular saws.

Once a product is completed, it is packaged and stored for shipment or direct sale. Limestone of insufficient quality or size for current demand is stocked on-site for future use, crushed for use in paving and construction applications, or stored for site reclamation activities.

1.1.5 Importance of limestone

Because limestone deposits are widely distributed throughout the world, a high proportion of humanity has ready access to the material. No reliable figures appear to have been published for the worldwide use of limestone, but Oates (1998) estimates that it is about 4,500 million tonnes per annum (tpa) and plays an important role as an essential raw material for many industries.

In most countries, the major uses of limestone are as an aggregate in construction and building and as a primary raw material for the production of cement. The amount of limestone used in construction and building varies widely from one locality to another and depends on its availability and cost relative to other aggregates, such as gravel and crushed hard rocks. Similarly, Dolley (2007) pointed out that limestone is most commonly employed as rough block for building and construction. Additionally, it is used as dressed stone in various applications including curbing, paneling, veneer, and tile. Its various functions cause a major expansion in the demand for limestone.

The proportion of limestone quarried that is used in construction and building is also affected by availability and cost. In many countries, the grade is around 40 to 50 % CaCO_3 ; however, limestone is widely available with fairly high grade ($> 70\%$), for example, such as in Japan, USA and UK. Some limestones contain over 95 % CaCO_3 . Such “chemical grade” materials are particularly suitable for lime production, flue gas desulfurisation and a range of other processes (*e.g.*, glass-production and metals-refining industries) as mentioned by Oates (1998).

Very finely divided limestones (whiting) and precipitated calcium carbonate are used as fillers. While the tonnages involved are minute when compared with the total, they are very high added-value products that play important roles in a wide range of industries.

When limestone is not an essential raw material for the production of cement, it is generally the cheapest source of calcium oxide. On the basis of the global production of cement, the limestone used in its production probably amounts to about 1,500 million tpa, or one third of the total extracted (Oates, 1998).

According to the mineral industry of Japan, Japan has considerable resources of industrial minerals especially carbonate rocks although it has negligible mineral resources of energy and ferrous and nonferrous metals. It was reported that Japan was one of the world’s top limestone producers in 1999 (Wu, 1999).

1.2 Aquifer system in limestone quarry

Limestones, the carbonate rocks, frequently form productive aquifers and consist of recrystallized biological material with a high porosity and a low permeability. Groundwater flow is then restricted to more permeable fracture zones or cracks produced by carbonate dissolution (Appelo and Postma, 2005). Dissolution over periods of thousands of years may result in severe erosion and form such openings, sinkholes, karst and cave features (Figure 1.3).

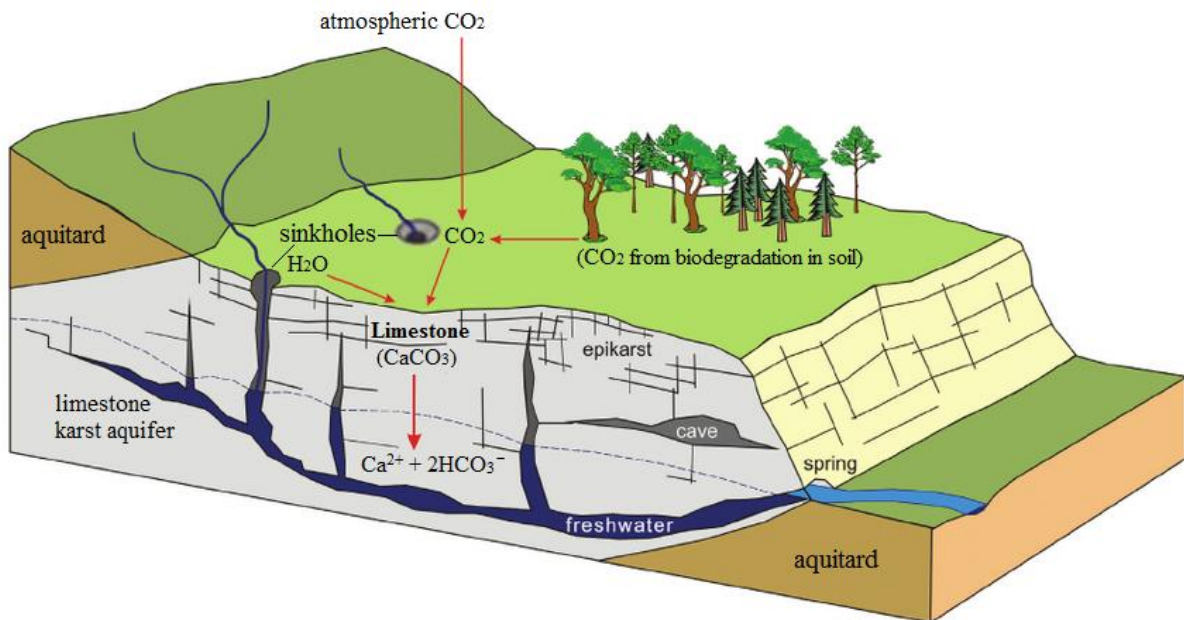


Figure 1.3 Schematic illustration of a limestone karst system and its relevant processes (modified after Goldscheider *et al.*, 2007)

1.2.1 Groundwater management

Managing groundwater is a grand challenge problem (Konikow and Kendy, 2005) and has become one of humanity's foremost priorities. Groundwater resources are often hidden and more difficult to conceptualize, even though surface water resources are somehow typically managed and relatively well understood.

Extraction of limestone from below the natural water table may produce large volumes of groundwaters from aquifers discharged into local rivers and channels and may cause the salinization of the streams (Iwanoff, 1998). Thus, groundwaters discharged from limestone aquifers or from limestone quarrying basically result in environmental impact but may not present a significant environmental hazard (Oates, 1998) such as those from heavy metal mines. In addition, those groundwaters are mostly alkaline as a result of dissolved calcium carbonate and produce higher water hardness (Todd and Mays, 2005). On the other hand, the presence of groundwaters potentially causes rock slope issues, which is a part of geotechnical and safety engineering.

Effective groundwater management is, therefore, relatively important for both environment and safety management in mine sites. Primarily, the focuses of groundwater chemistry, geochemical processes and factors influencing groundwater quality within the system, and groundwater effects on the stability of rock slopes are addressed as in the following sections.

1.2.2 Groundwater chemistry

Groundwater chemistry is relevant to all users of groundwater resources, whether it be for drinking, irrigation, industrial, or other purposes. Chemistry is also central to understanding the fate of groundwater contamination and how to remediate contamination, whereas characterizing and predicting chemical processes are some of the most challenging problems in groundwater science (Fitts, 2002).

In groundwater, only seven solutes make up nearly 95 percent of all water solutes (Herczeg and Edmunds, 1999; Runnells, 1993). These solutes are Ca, magnesium (Mg), sodium (Na), potassium (K), chloride (Cl), sulfate (SO_4), and bicarbonate (HCO_3). Although many sources and reactions cause changes of the concentrations of these solutes, the predominant sources of these solutes to groundwater would basically include (1) the dissolution of limestone (calcite, CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) for Ca, Mg, and HCO_3 ; (2) the dissolution of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) for Ca and SO_4 ; (3) the dissolution of halite (NaCl) for Na and Cl; and (4) ion exchange reactions on the surfaces of some clay minerals whereby Na is released to the water in exchange for Ca or Mg (Anderholm, 1987; Plummer *et al.*, 2002).

1.2.3 Geochemical processes and factors influencing groundwater quality

Geochemical processes occurring within groundwater and reactions with aquifer minerals have a profound effect on water properties. These geochemical processes are responsible for the seasonal and spatial variations in groundwater chemistry of an area. Geochemical processes change the groundwater type during its flow from the recharge area. Various geochemical mechanisms result in the change of groundwater chemical composition.

The geochemical properties of various groundwater bodies are controlled by the chemistry of water in recharge areas as well as by different geochemical processes taking place in the subsurface. The quality of water along the course of its underground movement is thus dependent upon the chemical and physical properties of the surrounding rocks, quantitative and qualitative properties of through-flowing water bodies, and products of human activity (Matthess, 1982). According to Mercado *et al.* (1977), a hydrogeochemical system is a complex natural framework including liquid, gaseous and mineral phases. The input of solutes and the physico-chemical reactions occurring in the hydrochemical system of an aquifer define the chemical properties of its groundwater.

Open geochemical systems such as aquifers are in direct hydrological and thermodynamic contact with their surroundings. The chemical composition of groundwater is controlled by the inflow and outflow of solutes across the boundaries of the system (Mercado *et al.*, 1977; Hem, 1985), and by various chemical processes happening within the aquifers. Some of the processes controlling the chemical composition of major dissolved salts of the waters of the earth have been discussed by Mackenzie and Garrels (1965), and Gibbs (1970).

The geochemical composition of groundwater is determined by a number of factors. These include the mineralogy of the rock types forming catchments or aquifers, overlying land uses, proximity to the coast, source of recharge water, soil type, aquifer structure and the time when water has been in underground away from atmospheric processes.

On the one hand, Appelo and Postma (2005) mentioned that the groundwater quality may change during the exploitation or it may be affected by human activities of which the impact is not always immediately evident.

On the other hand, one of the major factors controlling the geochemistry of groundwaters is naturally occurring process and to understand groundwater geochemistry, it is necessary to be familiar with them. For example, one of the peculiarities of New Zealand aquifers is the localized differences in groundwater quality. This reflects New Zealand's unique combinations of geology, source of recharge water, subsurface flow patterns and overlying land use (Rosen, 2001; Daughney and Reeves, 2005). As another example, groundwater in Marlborough that has been recently recharged, either by rain or river water, will have a similar chemistry to its source water. It is only groundwater that becomes isolated from the oxidizing influence of the atmosphere, and over time naturally evolves, so it becomes geochemically distinct (Morgenstern *et al.*, 2009; Botting, 2010).

Generally all aquifer recharge water is chemically dilute with naturally low concentrations of dissolved salts. This changes as rainwater leaches natural salts from the soil on its downward path to the water table. Also, the acidification of new recharge water lowers the pH of groundwater once it arrives at the water table. So, the change in groundwater chemistry commonly occurs as the effects of a variety of geochemical processes (Freeze and Cherry, 1979).

1.2.4 Groundwater effects on the stability of rock slopes

Mining operations from prospecting to excavation cause ecological problems from erosion, formation of sinkholes, biodiversity loss, heavy metal contamination (Kraus and Wiegand, 2006) and rock slope failures under the effects of groundwater.

Groundwater is one of the most important factors in the slope stability analysis. Pore-water in rock can strongly influence the physical (*e.g.*, rock strength) and chemical properties (*e.g.*, mineral dissolution) especially for limestone consisting largely of moderately water-soluble minerals like calcite. Changes in pore-water pressures can directly impact the effective stresses, which in turn, affect both the shear strength and consolidation behaviour of rock (Beale *et al.*, 2013), particularly under higher pore-water pressure (Patton and Deere, 1971). Therefore, the study of groundwater is important in the solution of many geotechnical problems, especially those concerning the stability analysis of slopes and also retaining structures.

Failure of rock slopes, both natural and man-made, during or shortly after rainfall is a commonly occurring phenomenon. Such rainfall-related failures are often associated with tropical areas, where intense rainfall may occur seasonally, and the rocks are weathered. Under these conditions, infiltration may result in a large volume of water entering into unsaturated zones or occupying the fractures within rock slopes and can significantly reduce the stability of rock slopes. Water pressure acting within a discontinuity reduces the effective normal stress acting on the plane, thus reducing the shear strength along the plane (Read *et al.*, 2013). If a load is applied at the top of a slope, the pore-water pressure increases. Such a load can lead to immediate failure of the slope if it exceeds its shear strength of the slope. It means that water filling in discontinuities can result in lowering of stability conditions for natural or artificial slopes.

In other cases, Bjerrum and Jorstad (1964) and Lumb (1975) presented a statistically high correlation between infiltration events and slope failures on weathered and unweathered rock slopes. Also, horizontally bedded slopes in which the principal direction of anisotropy is horizontal do not develop pore-water pressure as great as slopes where the bedding and the principal direction of anisotropy dip parallel to the slope face (Sharp *et al.*, 1972).

1.3 Statement of the problem and objectives of the study

In general, rock slope failures are the major cause of deaths and serious injuries in limestone mines (Oates, 1998). After a limestone deposit is mined out, a huge final slope is left in the mountainous area. Therefore, slope instability is a major problem, not only from the viewpoint of safety but also from the environmental control standpoint. For instance, a slope at the Kagemori limestone quarry collapsed in 1973 with 300,000-400,000 m³ of fallen rock debris and this accident stimulated serious consideration of slope stability problems in the limestone industry of Japan (Yamaguchi and Shimotani, 1986). Meanwhile, an open-pit limestone quarry in Chichibu city encounters rock displacement and crack growth which can lead to rock slope failures.

Although mechanical properties of limestone including the effects of groundwater level and flow have been adequately investigated in previous researches, monitoring and

assessment of geochemical properties and geochemical processes of groundwater for the stability of rock slopes are rarely reported. The detailed investigation of geochemical data of groundwater would assist in the identification of geochemical processes responsible for variations in groundwater chemistry. The important processes possibly identified are such mixing of different groundwaters, water-rock interaction, mineral equilibria and reactions, dissolution and deposition, movement and residence time of groundwater (timescale of groundwater or groundwater age).

In this dissertation, the results of groundwater monitoring of the open-pit limestone quarry in Chichibu city of Saitama prefecture, Japan for 2 years including in situ measurement of groundwater samples, chemical analyses in the laboratory, geochemical modeling, statistical analyses, and measurements of tritium were carried out. The objectives of this entire research are as follows:

- i. to investigate groundwater characteristics, evolution and their connections to rock slopes
- ii. to elucidate the contributions of water-rock interaction to slope stability in a limestone quarry, and to classify groundwater samples and their sources using geochemical and statistical analyses
- iii. to estimate and verify possible mixing of groundwaters within the rock layers using geochemical models, to define groundwater ages by tritium analysis, and to clarify sensitive zones affecting rock slopes for improvement on the slope stability.

1.4 Outline of the dissertation

This dissertation is divided into five chapters which are subjected to discuss and elaborate the entire research work. Here is the brief view of each chapter:

Chapter 1: covers the general introduction of limestone overview, aquifer system in limestone quarries, statement of problem and objectives of the research, and finally thesis overview of the whole research work.

Chapter 2: discusses groundwater characteristics, evolution and their connections to rock slopes in a limestone quarry.

Chapter 3: elucidates the contributions of water-rock interaction to slope stability in the limestone quarry and the classification of groundwater samples and their sources using geochemical and statistical analyses.

Chapter 4: elaborates the mixing estimation of groundwaters within the rock layers using geochemical models, the groundwater age-dating by tritium analysis, and the identification of sensitive zones affecting rock slopes for improvement on the slope stability.

Chapter 5: concludes the fulfilment of the research work based on the applied methodology, especially the achievement of research objectives, and suggests some missing points in order to enhance the further research.

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CHAPTER 2

GROUNDWATER CHARACTERISTICS, EVOLUTION AND THEIR CONNECTIONS TO ROCK SLOPES

2.1 Introduction

Japan has large reserves of limestone, an important industrial mineral quarried for cement productions, construction aggregates, food additives and consumptions in iron and steel industries (Kuo, 2012). Because of these demands, large-scale limestone quarries are still in operation. Limestone also often forms productive aquifers under favorable conditions for groundwater abstraction. The density, porosity and permeability of limestone aquifers basically depend on the degree of consolidation of sediments and development of permeable zones after deposition. Calcite (CaCO_3) is the main mineral component of this rock, which is moderately soluble in water (Plummer *et al.*, 1978). The dissolution of this rock produces "hard" groundwater and with time, increases the pore-space and permeability of the rock (Todd and Mays, 2005). Prolonged dissolution may result in the development of karst terrain, subterranean drainage through sinkholes, caves and various features. Aside from limestones, sedimentary rocks such as mudstones and sandstones contain carbonate minerals as accessory minerals or as cement-like phases around more inert grains (Tabelin *et al.*, 2012; Tabelin *et al.*, 2014). Because of this, the effects of carbonate-mineral dissolution on water compositions are quite conspicuous. According to Appelo and Postma (2005), the high values of total dissolved solids (TDS) in groundwater worldwide are mainly related to the increase in concentrations of calcium ion (Ca^{2+}) and bicarbonate ion (HCO_3^-), which are predominantly due to carbonate dissolution.

From another perspective, most of the limestone quarry sites in Japan are located in mountainous topography. Existence of groundwater in the quarry sites potentially causes slope stability problems (American Society for Testing and Materials, 1997), so groundwater levels are closely monitored and continuously reduced during mining and quarry operations. As rock slopes get larger in quarry sites, they become more important to keep them stable for safety and economic purposes. However, there have been several rock slope failures in limestone quarries in Japan (Yamaguchi and Shimotani, 1986). In 1973, a slope at the Kagemori limestone quarry near this study site collapsed with 300,000–400,000 m^3 of fallen rock debris. This accident sparked the start of serious considerations of slope stability problems in the limestone industry of Japan. To avoid the repetition of such disastrous events, continuous monitoring of hydrogeological and mechanical properties of rock slopes has been conducted (Matsuda *et al.*, 2002; Kodama *et al.*, 2004). Slope collapses are triggered by many factors; groundwater flow and its potentiometric level are two of the most important factors (Ulusay *et al.*, 2014). In particular, intense rainfall and the associated rapid groundwater flow have been strongly correlated to the instability of slopes because the abrupt changes of groundwater level increase pore-water pressures near the slide surface (Sjöberg, 1999; Yoshida and Nozaki, 2008; Yoshida *et al.*, 2008). Záruba and Mencl (1976) found that two beds along which a sliding plane was formed had different values of electrical potential due to changes in their water contents. They explained that the increase in water content led to slope movement using electro-osmotic techniques. This means that understanding of rainwater

infiltration and groundwater flow in limestone quarries is crucial in the evaluation of slope stability.

In this study area, rock slopes are being deformed due to rising groundwater levels after intense rainfall events (Kondo *et al.*, 2016; Ozawa *et al.*, 2016). To mitigate this problem, groundwater in each geological formation is abstracted periodically to reduce the levels of groundwater. However, monitoring results of crack growth indicated that this approach was not enough to stop the deformation of rock slopes. One important geochemical process that was overlooked in the planning of the mitigation approaches for this site was the mixing of groundwater within three geological formations, which could lead to localized disequilibrium conditions that may enhance the dissolution of calcite and weaken the rock strata.

Although hydrochemical impacts of limestone quarries on the environment have been well investigated (Naja *et al.*, 2011), monitoring and assessment of the geochemical evolution of groundwater for the purpose of stabilizing rock slopes are rarely reported. Groundwater monitoring including its chemical properties is critical in explaining how environmental factors and processes influence the dissolution of calcite. Changes in geochemical properties of groundwater could provide valuable information, which may help in recognizing potentially weak zones within the geological formations (*e.g.*, different rock layers, depths and discontinuities). With regards to the above mentioned issues, the objectives of this chapter are to investigate the characteristics of groundwater, the geochemical evolution of groundwater and their connection to the rock slopes of the open-pit limestone quarry based on variations of groundwater chemistry in groundwater flow paths.

2.2 Materials and methods

2.2.1 Site description and sample collection

The open-pit limestone quarry of this research is located in the mountainous region of Chichibu city, Saitama prefecture, Japan (Figure 2.1). The original elevation to the top of the mountain is 1,336 m. The quarry is designed with bench height, width and slope angle of 10 m, 2.5 m, and 60°, respectively. The final slope angle of 45°–50° is used at higher elevations (>1,000 m) while greater steep angle of 70°–80° is utilized at lower elevations (<1,000 m) (Figure 2.2). This quarry is mainly composed of three rock strata: limestone layer as covering rock, interbedded layer of limestone and slaty greenstone underlying the covering rock, and slaty greenstone layer as basement rock (Figure 2.3). Limestone in the covering layer is mostly grayish to white in color, microcrystalline and compact. Limestone in this area was formed during the Triassic period (Fujinuki, 1983; Hayashi *et al.*, 1990), which covers the northern half of the mountain extending 5 km east-westwardly with about 500 to 700 m in thickness. The limestone deposit lies monoclinically with a strike of N70°E and dip of 45° to 80° north. The covering layer is composed predominantly of high quality limestone with small amounts of black limestone or shale embedded within the layer. In the interbedded layer, limestone and slaty greenstone are both cryptocrystalline, and they are interbedded or sometimes mixed together with thicknesses ranging from centimeters to several meters. Multi-breaking zones are distributed in the interbedded layer, which were probably formed by repetitive fault movements. Slaty greenstone of the basement rock has a dark green to red purple color and was formed by alteration of basaltic rocks. Although the slaty greenstone at greater depth is solid, the rock immediately below the interbedded layer has cracks, joints and weak faces because of structural movements and groundwater flow, and its weaker mechanical properties have been partly recognized. Slaty greenstone collected near the interbedded layer is brittle and easily peeled-off into flat pieces due to the development of flake-like structure (Committee on the long-wall rock slopes, 2013).

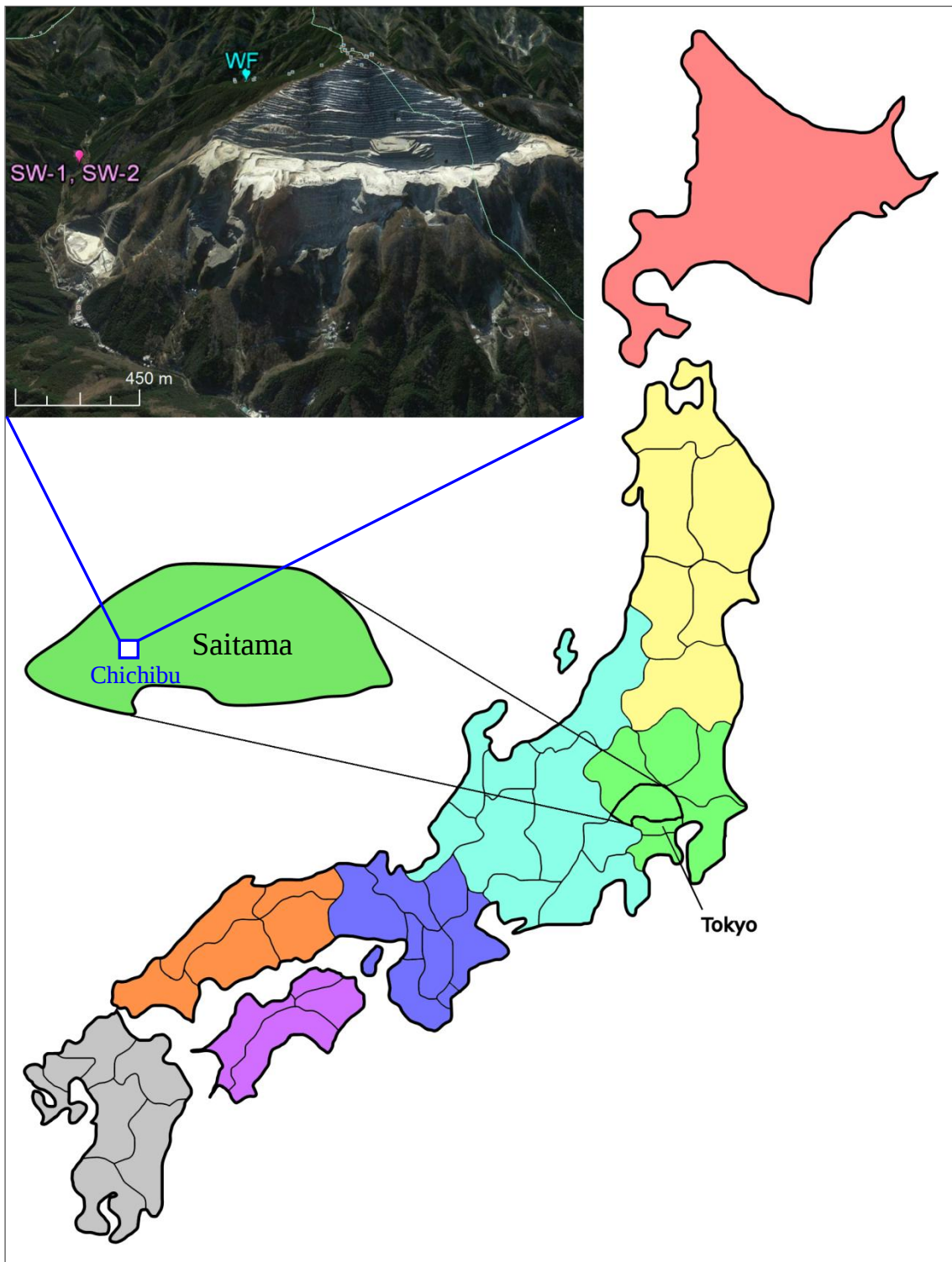


Figure 2.1 Map of study area (Inset from Google earth (February 15, 2017); SW-1 and SW-2: sampling points of shallow groundwater from springs at an elevation of 478 m; WF: sampling point of surface water at an elevation of 842 m)

Representative samples of limestones in the covering and interbedded layers as well as slaty greenstones in the interbedded and basement layers were collected to characterize their mineral and chemical properties. Mineral components of these rock samples were identified by X-ray powder diffraction (XRD, MultiFlex, Rigaku Corporation, Japan), and their

chemical compositions were determined by X-ray fluorescence (XRF, Spectro Xepos, Rigaku Corporation, Japan).

The cross sectional and plan views of the limestone quarry with sampling points of groundwater are illustrated in Figures 2.3 and 2.4, respectively. Underground tunnels were excavated to monitor the geological and hydrogeological conditions inside the quarry. Several boreholes were drilled upward to drain and collect groundwater samples as well as to monitor groundwater levels. Ten groundwater sampling campaigns were conducted from December 2014 to August 2016. During each sampling campaign, 13 groundwater samples in the limestone layer (L-1–L-11, LP-1 and LP-10), 4 groundwater samples in the slaty greenstone layer (S-1–S-4), and 2 shallow groundwater samples from the springs (SW-1, SW-2) were collected. One surface water (WF) sample was also collected in August 2015 after a strong rainfall event. The sampling and analysis of shallow groundwater and surface water located near the quarry (Figure 2.1) were carried out to compare with the quality of the groundwater in the quarry. In total, 164 water samples were collected in and around the study area.

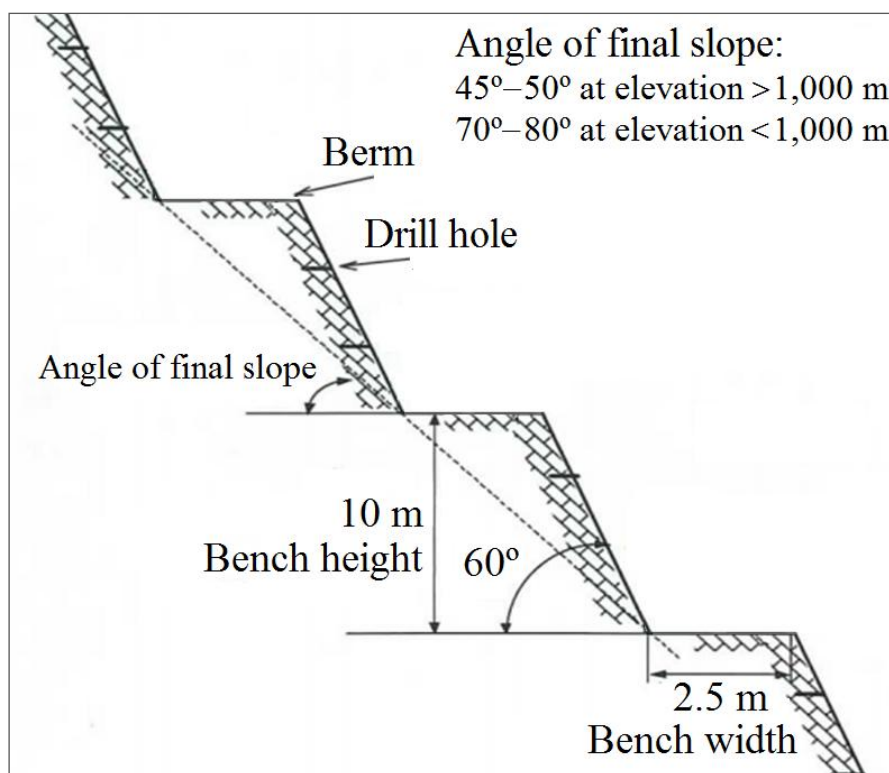


Figure 2.2 Bench design of the limestone quarry

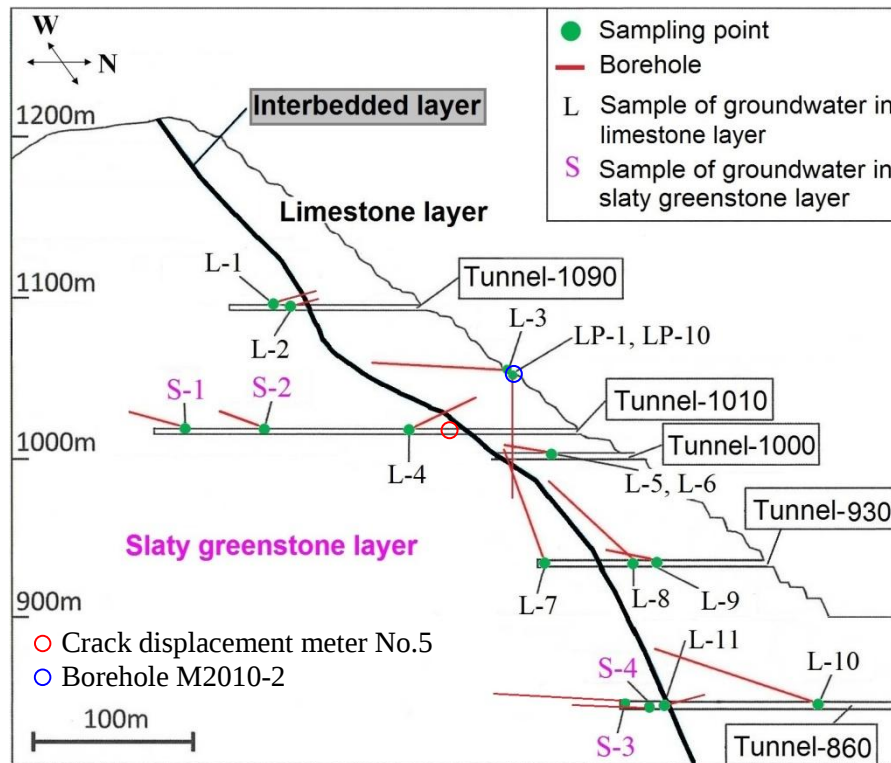


Figure 2.3 Cross sectional view of the limestone quarry with indication of sampling points of groundwater

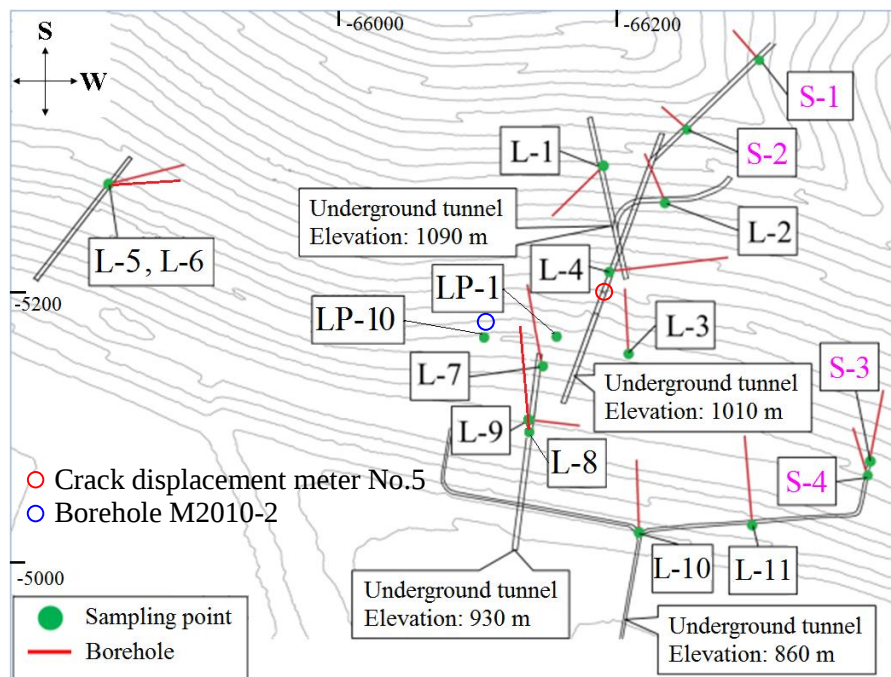


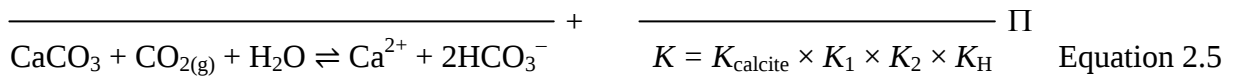
Figure 2.4 Plan view of the limestone quarry with indication of sampling points of groundwater

2.2.2 Groundwater monitoring and geochemical modelling calculations

Geochemical properties of groundwater were monitored periodically. Temperature, pH, electrical conductivity (EC) and oxidation-reduction potential (ORP) of water samples were measured in situ. Their flow rates were measured using the volumetric method by recording the volume of water flowing into a graduated cylinder in a specific length of time, and the measurements were repeated 3 times for each sampling point to obtain the accurate flow rate. Groundwater samples were divided into two portions on site in preparation for the chemical analysis. The first one was unfiltered, which was stored in 250 mL bottles (with no visible bubble, tightly capping and sealing with plastic tape to avoid degassing or in contact with air) while the second one was filtered through 0.45 μm Millex® membrane filters (Merck Millipore, USA) and stored in 100 mL bottles. The alkalinity was measured for unfiltered samples by titration with 0.01 M sulfuric acid in the laboratory immediately after receiving the samples from the quarry. Concentrations of dissolved ions and trace elements were measured for filtered samples using ion chromatographs (ICS-90 and ICS-1000, Dionex Corporation, USA) and inductively-coupled plasma atomic emission spectrometer (ICP-AES, ICPE-9000, Shimadzu Corporation, Japan), respectively. Ion chromatographs and ICP-AES both have margins of error about 2–3% with the detection limit of approximately 0.01 mg/L.

PHREEQC version 3 (Parkhurst and Appelo, 2013) was used to calculate changes in the partial pressure of carbon dioxide (P_{CO_2}) and the saturation index of calcite (SI_{calcite}) based on the measured pH, pe (calculated from ORP), temperature, alkalinity, concentrations of dissolved ions (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , Cl^- and NO_3^-) and some elements (Si, Fe and Al) of water samples.

$P_{\text{CO}_2(\text{g})}$ is derived from the combination of the dissolution reaction of calcite as following:



$$[\text{Ca}^{2+}][\text{HCO}_3^-]^2 / P_{\text{CO}_2(\text{g})} = K \quad \text{Equation 2.6}$$

where K_{H} is Henry's constant, and K_{calcite} , K_1 , K_2 and K are the equilibrium constants of each reaction ($K = 10^{-6} \text{ atm}^{-1}$ at 25 °C). The $P_{\text{CO}_2(\text{g})}$ is in atm unit, and $[\text{Ca}^{2+}]$ and $[\text{HCO}_3^-]$ are the activities in the water sample. Equation 2.5 is the most representative and fundamental for understanding the behaviour of CaCO_3 dissolution and precipitation in nature (Garrels and Mackenzie, 1967; Langmuir, 1971; Appelo and Postma, 2005).

From the definition, however, the saturation index of calcite is computed from Equation 2.1 and defined as following:

$$SI_{\text{calcite}} = \log (IAP/K_{\text{calcite}}) = \log ([\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{\text{calcite}}) \quad \text{Equation 2.7}$$

where IAP is ion activity product for the calcite mineral dissolved into water.

2.3 Results and discussion

2.3.1 Mineralogical and chemical properties of rock strata

Limestone in both the covering and interbedded layers is mainly composed of calcite (Table 2.1). Slaty greenstone in the interbedded and basement layers also has similar mineralogical compositions consisting of quartz, albite, calcite, chlorite and hematite. The main difference between these two rock formations is that the slaty greenstone of the basement rock layer has negligible amounts of calcite. The slaty greenstone in the interbedded and basement layers contains 38.5 to 39.7 wt.% of SiO₂ while CaO in limestone of the covering and interbedded layers amounts to 54.6 and 52.9 wt.%, respectively, which conforms well to geological description of high quality of limestone (Table 2.2).

Table 2.1 Mineral compositions of rock strata

Sample no.	Rock type	Identified minerals
1	Limestone (Covering rock)	Calcite
2	Limestone (Interbedded layer)	Calcite
3	Slaty greenstone (Interbedded layer)	Quartz, albite, calcite, chlorite, hematite
4	Slaty greenstone (Basement rock)	Quartz, albite, chlorite, hematite

Table 2.2 Chemical compositions of rock strata

Sample no.	1	2	3	4
SiO ₂	0.24	1.58	38.51	39.71
TiO ₂	0.02	0.08	2.25	3.39
Al ₂ O ₃	0.42	1.03	14.31	15.32
Fe ₂ O ₃	0.25	0.47	13.26	15.65
MnO	0.003	0.001	0.21	0.24
MgO	0.52	1.07	9.39	8.30
CaO	54.62	52.91	7.54	8.04
Na ₂ O	0.01	0.02	1.81	2.40
K ₂ O	< 0.01	< 0.01	0.05	0.10
P ₂ O ₅	0.03	0.02	0.45	0.45
LOI	42.84	42.12	11.62	5.04
Total	98.95	99.30	99.40	98.64

※Unit: wt.%

2.3.2 Preliminary results of rock deformation at the site

Ozawa *et al.* (2016) and Kondo *et al.* (2016) reported that there were many factors affecting the deformation of the remaining wall rock in the study area and their combined effects appeared in the total displacement of the slope. During the event of intense rainfall, for example, there was a tendency for crack displacement to rapidly increase with the rise in groundwater level (see Supplementary Figs. 1 and 2 in Appendix A). To reduce slope displacements, embankments to support the remaining wall rock have been constructed and part of the mine has been paved to eliminate rainwater infiltration.

2.3.3 Groundwater monitoring

Table 2.3 summarizes the geochemical properties of all water samples collected at the site including the maximum, minimum and arithmetic mean of the concentrations of major ions and some minor elements. Among the parameters, the flow rate in the covering layer had larger fluctuations than that in the basement rock because the hydraulic conductivity of former (4.1×10^{-4} cm/s) was about two orders of magnitude higher than the latter (4.2×10^{-6} cm/s).

Table 2.3 Flow rate (L/min), pH, temperature (T, °C), EC (mS/m), ORP (mV), concentrations of major and minor ions, and trace elements (mg/L) of water samples collected from December 2014 to August 2016

Parameters	Limestone layer (110 samples)			Slaty greenstone layer (35 samples)			Springs (18 samples)			Surface water (1 sample)
	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	
Flow rate	299	0.01	7.31	69.9	0.02	17.3	73.4	2.37	33	NA
pH	8.43	7.77	8.09	8.64	7.98	8.37	7.56	6.79	7.16	7.84
T	17.9	6	10.23	10.5	8.8	9.77	14	9.4	11.72	15.8
EC	26.5	16	19.5	16.9	11.1	13.5	12.1	10.3	11.2	11.2
ORP	241	91	163	207	118	165	271	160	212	137
K ⁺	0.78	0.04	0.24	0.33	0.12	0.23	0.52	0.42	0.49	0.21
Na ⁺	3.06	0.35	1.45	2.27	1.65	1.92	3.88	3.24	3.49	1.86
Ca ²⁺	57.1	23.5	41.8	32.9	17.5	24.8	17.6	13.2	15.5	15.4
Mg ²⁺	4.23	0.21	1.27	3.48	2.33	2.79	3.06	2.48	2.78	4.81
Cl ⁻	4.91	0.52	1.02	1.49	0.96	1.15	2.13	1.71	1.86	1.22
NO ₃ ⁻	8.98	0.42	1.08	5.53	4.05	4.67	8.66	5.52	6.22	6.36
SO ₄ ²⁻	21.4	2.47	10.02	4.9	3.87	4.2	11.9	10.4	11.0	4.83
HCO ₃ ⁻	122	86.4	107	93.2	56.4	71.5	48.3	33.9	41.3	58.3
Fe	0.094	<0.01	0.007	0.057	<0.01	0.006	0.052	<0.01	0.008	<0.01
Al	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Si	7.02	1.45	3.15	6.94	5.91	6.45	7.11	5.91	6.52	7.04

※NA: Not available (the flow rate was not measured due to its disseminated flow path)

Chemical properties of samples collected in August 2015 were plotted in the Piper diagram to characterize the hydrochemical facies of groundwater, springs and surface water (Figure 2.5). The results showed that Ca²⁺ and HCO₃⁻ were the major ions of groundwater in the covering and slaty greenstone layers. Shallow groundwaters from the springs and surface water were also Ca-HCO₃ type but with a slight change in ionic concentration percentage. These results suggest that the geochemistry of all water sources at the site is strongly influenced by calcite dissolution ($\text{CaCO}_3 + \text{CO}_{2(\text{g})} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$).

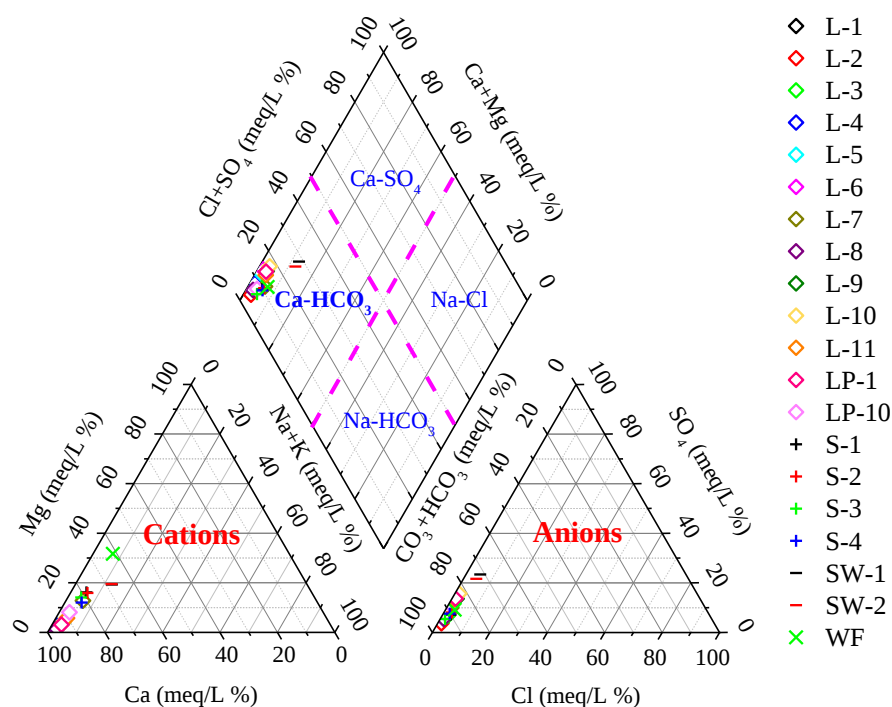


Figure 2.5 Representative Piper diagram of the water samples collected in August 2015

The hardness of groundwater in the covering layer (68.6 to 153 mg/L) was slightly higher than that in the basement rock (54.7 to 96.4 mg/L). In comparison, both groundwaters had higher hardness compared with the shallow groundwater and surface water (44.3 to 58.3 mg/L) (Figure 2.6). These results were expected because the covering layer is predominantly composed of calcite, which dissolves and releases Ca^{2+} into solution. According to Benefield and Morgan (1990), water is considered “soft” if the hardness is less than 75 mg/L and “hard” when hardness exceeds 150 mg/L. Most of the groundwater samples in the covering layer had hardness values between soft and hard while the shallow groundwater, surface water and most of the groundwater samples in the slaty greenstone layer were soft except groundwater samples S-3 (high water hardness in some periods of sampling) and S-4. In the slaty greenstone basement layer, the hardness values of samples S-3 and S-4 were fairly higher than those of samples S-1 and S-2, whereas the hardness values of L-7 and L-11 were generally lower than those of the groundwater in the limestone layer. These suggest that groundwater collected at L-7, L-11, S-3 and S-4 may originate from mixing of groundwater from the covering and basement rock layers (Table 2.3).

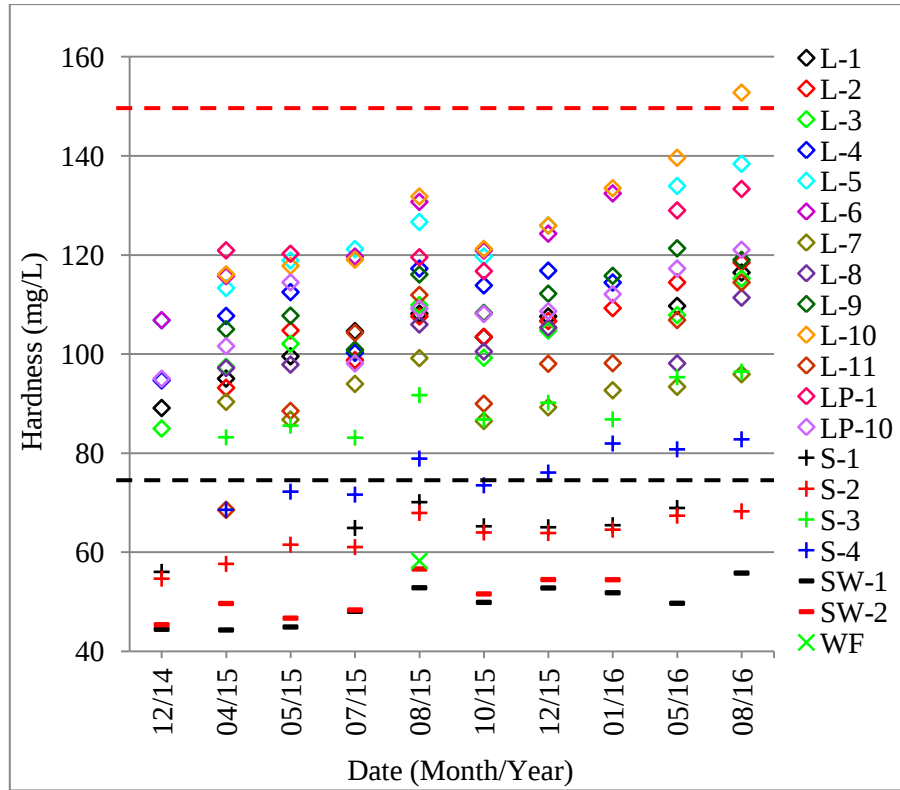


Figure 2.6 Hardness of water samples collected from December 2014 to August 2016 (— —: soft groundwater if hardness below the black-dashed line; — —: hard groundwater if hardness above the red-dashed line)

Ionic strengths of the samples ranged from 2.5×10^{-3} to 4.4×10^{-3} M in the covering layer, 1.9×10^{-3} to 2.9×10^{-3} M in the slaty greenstone layer and 1.7×10^{-3} to 2.1×10^{-3} M in the springs and surface water (Figure 2.7). This indicated that the dissolved ions of groundwater in the covering layer were higher than those in the slaty greenstone basement layer, shallow groundwater and surface water. Based on this higher ionic strength, the EC and TDS values of groundwater samples in the limestone layer were also higher than the other samples because ionic strength is positively correlated to EC (Snoeyink and Jenkins, 1980), and EC is also highly correlated to TDS (Freeze and Cherry, 1979; Hem, 1985). It is noticeable that samples collected at S-3 and S-4 had moderately higher ionic strengths than those at S-1 and S-2 while those from L-7 and L-11 generally had lower ionic strengths than the other samples in the covering layer.

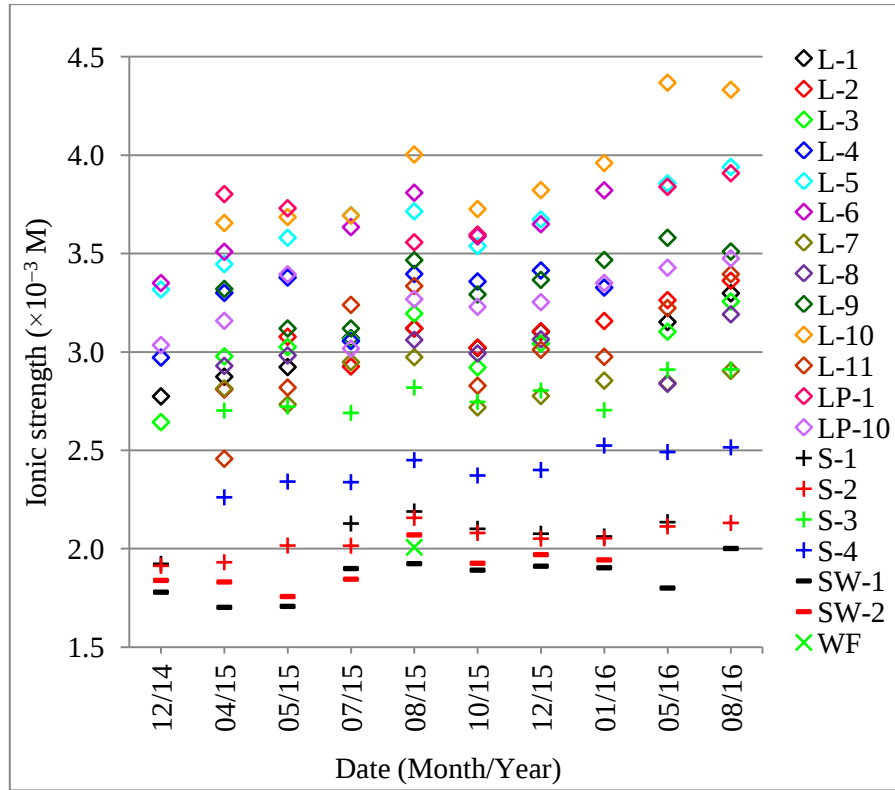


Figure 2.7 Ionic strength of water samples collected from December 2014 to August 2016

The Ca^{2+} concentrations of groundwater in the limestone layer ranged from 23.5 to 57.1 mg/L and were higher than those in the slaty greenstone layer, ranging from 17.5 to 32.9 mg/L (Figure 2.8). The lowest Ca^{2+} concentrations were observed in the shallow groundwater and surface water, which ranged from 13.2 to 17.6 mg/L. Furthermore, Ca^{2+} concentrations of samples from L-7 and L-11 were relatively lower than the other samples in the covering layer, which may be attributed either to the mixing of groundwater from the limestone and slaty greenstone layers or the effects of groundwater from the interbedded layer. The Ca^{2+} concentrations of groundwater in the limestone layer fluctuated more dramatically compared with those in the slaty greenstone layer. In the slaty greenstone basement layer, groundwater samples from S-3 and S-4 had higher Ca^{2+} concentrations compared with those from S-1 and S-2, which suggests that groundwater from the interbedded or limestone covering layer probably influences the groundwater from S-3 and S-4 in the basement layer.

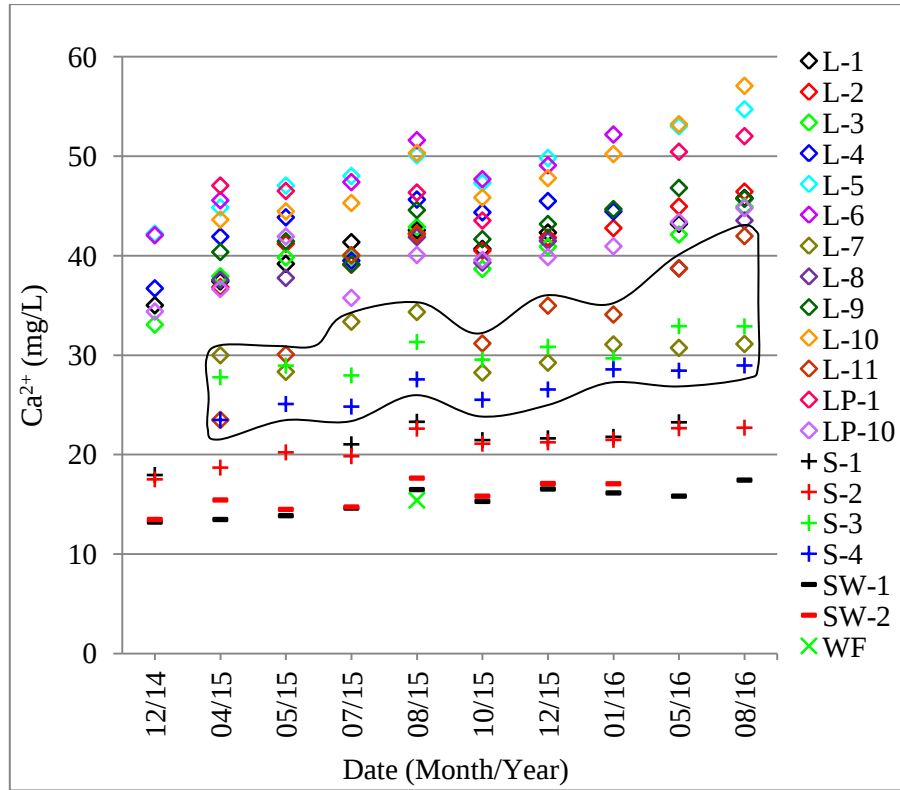


Figure 2.8 Distribution of Ca^{2+} concentrations of water samples collected from December 2014 to August 2016 (wavy line: circled area highlights the lower Ca^{2+} concentrations of samples L-7 and L-11 among the samples in the limestone layer and the higher Ca^{2+} concentrations of samples S-3 and S-4 among the samples in the slaty greenstone)

The alkalinity of groundwater in the limestone covering layer was the highest (1.42 and 2.02 meq/L) followed by groundwater in the slaty greenstone basement layer (0.92 to 1.53 meq/L) and shallow groundwater and surface water (0.56 to 0.96 meq/L) (Figure 2.9). This higher alkalinity of groundwater in the limestone covering layer conformed to their higher Ca^{2+} concentrations. The pH values of the groundwater in the limestone layer, groundwater in the slaty greenstone layer, and shallow groundwater and surface water were 7.77–8.43, 7.98–8.64 and 6.79–7.84, respectively. These pH ranges are between 6.3–10.3 (Morel and Hering, 1993) with their temperature conditions studied by Larson and Buswell (1943). Thus, HCO_3^- is suggested as the dominant carbonate species. In addition, the alkalinity (*i.e.*, HCO_3^- concentration) of samples from L-7 and L-11 was slightly lower than the rest of the samples from the limestone covering layer while those from S-3 and S-4 were higher among the samples from the slaty greenstone basement layer. In particular, the alkalinity of S-3 was nearly equal to those of L-7 and L-11, indicating that mixing of groundwaters from the slaty greenstone basement rock and limestone covering layer most probably occurred within their flow paths.

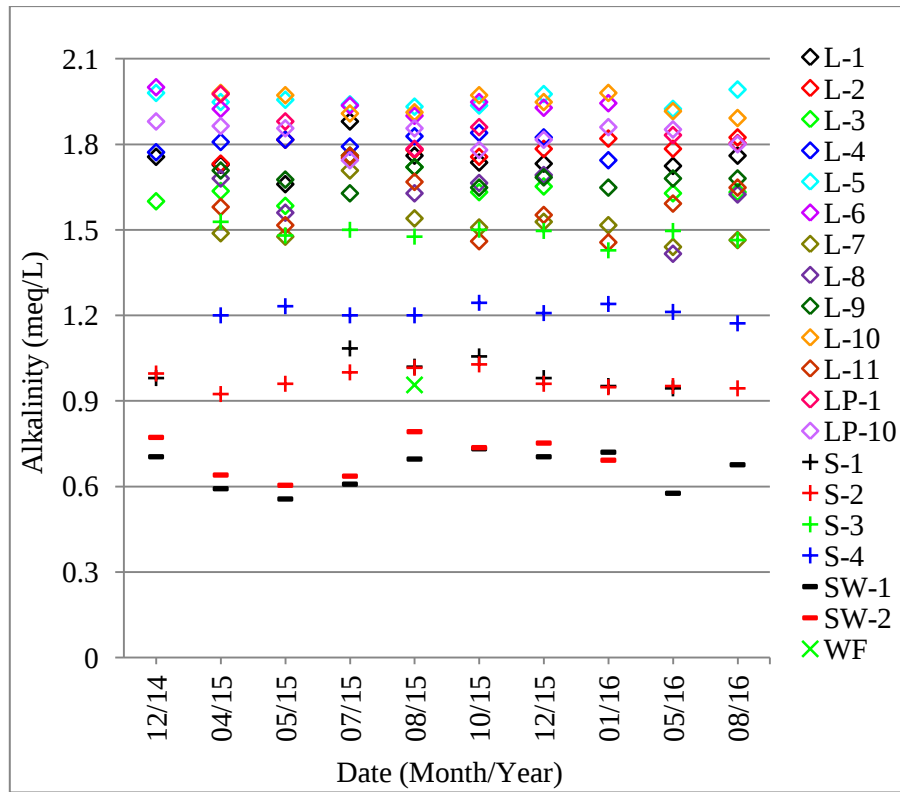


Figure 2.9 Distribution of alkalinity of water samples collected from December 2014 to August 2016

The relationship between alkalinity of water samples and flow rate is presented in Figure 2.10 (samples from LP-1, LP-10, S-3, SW-2 and WF were not included in the figure because they were pumped periodically or the flow rates were not measurable). The alkalinity of groundwater in the limestone covering layer tended to be constant irrespective of the flow rate, whereas that in the slaty greenstone layer gradually increased with the flow rate. However, the alkalinity of a few samples in the limestone layer, such as L-7 and L-11, significantly increased with flow rate (determination coefficients $R^2 = 0.75$ and 0.80 , respectively). This could be attributed to the mixing between groundwater from the limestone covering layer and slaty greenstone basement layer, which may have occurred in the interbedded layer. Also, the flow rate fluctuated depending on rainfall intensity, and groundwater flowing through the limestone covering layer likely became the dominant part of the mixture to form groundwater in L-7 and L-11 especially on the rainy day. For groundwater in the slaty greenstone basement layer, both alkalinity and flow rates were lower than those in the limestone layer. The alkalinity of groundwater in this layer slightly increased with flow rate, indicating that the groundwater from the interbedded layer or limestone layer with higher alkalinity may have been mixed especially at higher flow rates. On the other hand, the alkalinity was almost constant and independent of the flow rate in the shallow groundwater (SW-1).

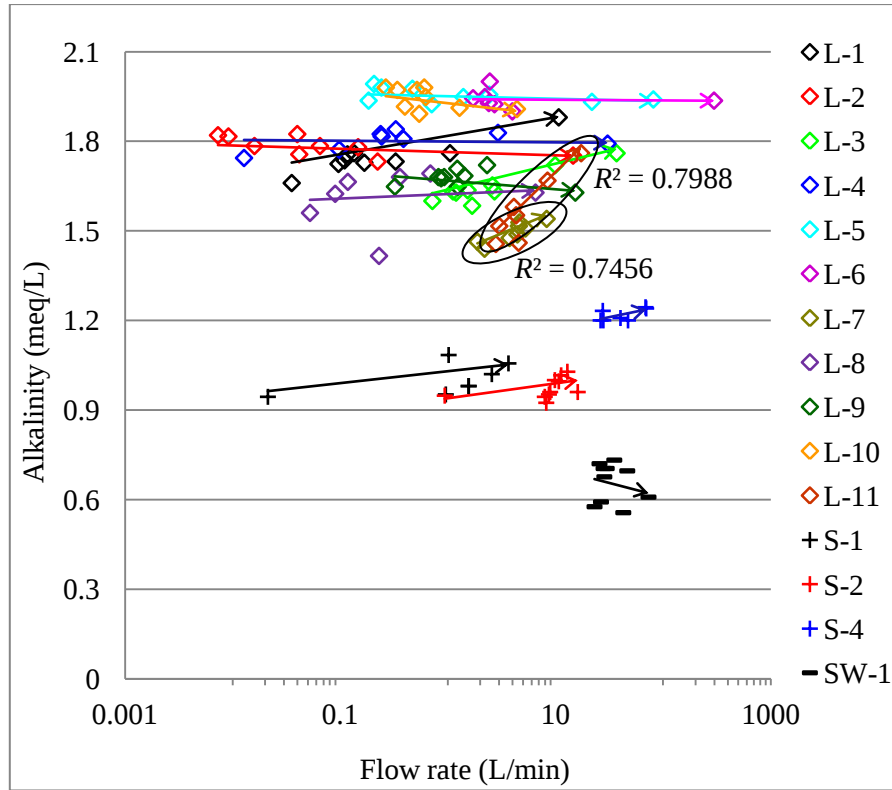


Figure 2.10 Alkalinity vs. flow rates of water samples collected from December 2014 to August 2016 (all arrows are the linear regression lines; 0: circled area indicates the positive correlation between alkalinity and flow rate for L-7 and L-11)

2.3.4 Geochemical evaluation

Chloride ion (Cl^-) is a conservative ion while $P_{\text{CO}_2(\text{g})}$ and SI_{calcite} vary and are controlled by reactive processes. Therefore, their variations are key indicators of calcite dissolution within groundwater flow paths, whereas the conservative Cl^- was not used for the evaluation of groundwater mixing because its concentration was very low, almost constant and apparently independent of the geological formations in the study area.

Figure 2.11 illustrates the distribution of $\log P_{\text{CO}_2(\text{g})}$ values of all water samples. The $\log P_{\text{CO}_2(\text{g})}$ values of groundwater in the limestone covering layer and surface water were greater than those in the slaty greenstone basement layer, but were smaller than those of the shallow groundwater. The $\log P_{\text{CO}_2(\text{g})}$ of the surface water was around -3.1, which was very close to the $\log P_{\text{CO}_2(\text{g})}$ of the atmosphere ($\log P_{\text{CO}_2(\text{g})} = -3.4$ at 25 °C). The surface water flows through the forested scree (for forested scree, the average $\log P_{\text{CO}_2(\text{g})} = -2$ according to Appelo and Postma, 2005), and gas-liquid interaction probably occurred, leading to a rise of $\log P_{\text{CO}_2(\text{g})}$. Shallow groundwater passes through the unsaturated zone where the P_{CO_2} of $10^{-1.5}$ atm has been reported, which is near the upper limit of respiration and organic matter degradation (Peyraube *et al.*, 2014). Consequently, the $\log P_{\text{CO}_2(\text{g})}$ values became larger and approached the normal range of $\log P_{\text{CO}_2(\text{g})}$ for shallow groundwater reported by Macpherson *et al.* (2008). The $\log P_{\text{CO}_2(\text{g})}$ values of groundwater in the limestone covering layer were higher than the $\log P_{\text{CO}_2(\text{g})}$ of the atmosphere, indicating an enhanced calcite dissolution in this layer. According to Appelo and Postma (2005), pH of water in equilibrium with calcite in an open system (*i.e.*, constant P_{CO_2}) is between 7.0 and 8.3 but would increase the range of

7.6–10.3 when CO₂ is not replenished (closed system). By considering the measured pH range of 7.77–8.43 in this study, groundwater in the limestone covering layer corresponded to an open system and is connected to the unsaturated zone with higher CO_{2(g)} than the atmosphere (Laursen, 1991). This relationship was evident in the lower log $P_{\text{CO}_2(\text{g})}$ values of groundwater in the limestone covering layer when the groundwater levels were low (*e.g.*, December 2015 and 2016) and higher log $P_{\text{CO}_2(\text{g})}$ values during rainy periods when the groundwater levels were higher (*e.g.*, July 2015). This difference could be explained by the uptake of carbon dioxide during the infiltration of rainwater through the unsaturated zone (Hanson *et al.*, 2000). The log $P_{\text{CO}_2(\text{g})}$ values in the slaty greenstone layer ranged from –3.2 to –4. The log $P_{\text{CO}_2(\text{g})}$ values of samples from S-1 and S-2 were always below –3.4, but those from S-3 and S-4 on the rainy day obviously exceeded –3.4 and were equal to the log $P_{\text{CO}_2(\text{g})}$ of some groundwater samples in the limestone covering layer. This indicates that on the rainy day, the groundwater of S-3 and S-4 would become the mixture of the groundwater in the slaty greenstone layer and that in the limestone covering layer or that in the interbedded layer.

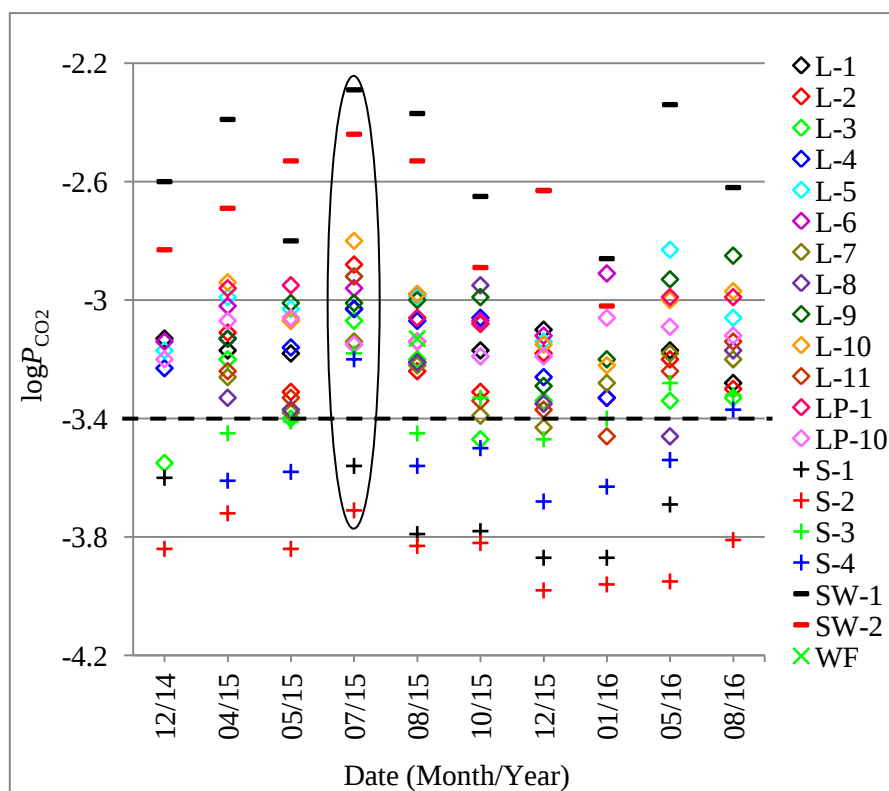


Figure 2.11 Distribution of log $P_{\text{CO}_2(\text{g})}$ of water samples collected from December 2014 to August 2016 (—: dashed line indicates the log $P_{\text{CO}_2(\text{g})}$ value of atmosphere; 0: circled area indicates the rainy day)

Calcite equilibrium calculations for groundwater are useful in predicting the presence of reactive calcite in the groundwater system (Acton and Barker, 1992; Deutsch and Siegel, 1997). By geochemical calculations using PHREEQC, the distribution of SI_{calcite} of all water samples is plotted in Figure 2.12. The SI_{calcite} of groundwater in the limestone covering layer was mostly greater than zero and was also higher than the SI_{calcite} of groundwater in the slaty greenstone basement layer, shallow groundwater and surface water. The SI_{calcite} values in all samples decreased in July 2015 while the log $P_{\text{CO}_2(\text{g})}$ increased because of intense rainfall

during this period (Figure 2.11). The recharge of rainwater could correspond to young groundwater in terms of residence time (Reilly *et al.*, 1994; Szabo *et al.*, 1996), and the groundwater-rainwater mixture during this period probably did not have sufficient time to equilibrate with calcite due to the faster flow rate. Paces (1975) and Merkel and Planer-Friedrich (2008) pointed out that the SI range of a mineral between -0.05 and $+0.05$ could still be considered in a state of equilibrium because of inherent uncertainties in the calculation of SI . This means that most of the groundwater samples in the limestone covering layer were supersaturated or in equilibrium with calcite except for those in July 2015. The groundwater samples in the slaty greenstone layer were dominantly in equilibrium or undersaturated with calcite, whereas shallow groundwater and surface water were always undersaturated with calcite.

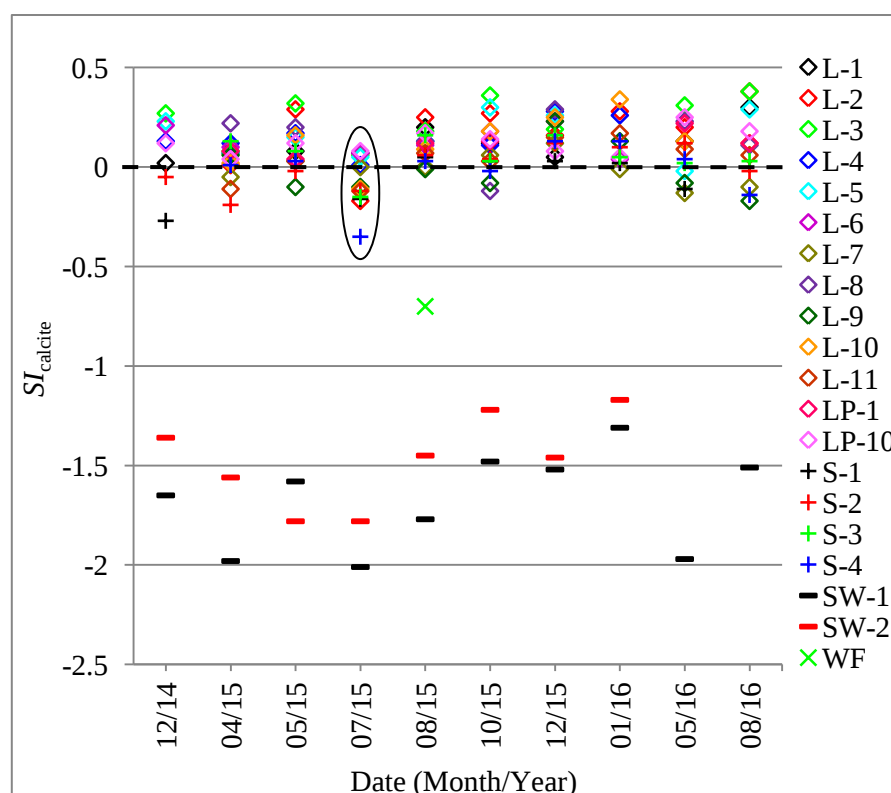


Figure 2.12 Distribution of SI_{calcite} of water samples collected from December 2014 to August 2016 (—: dashed line indicates the saturated condition of calcite mineral; 0: circled area indicates the rainy day)

Many fractures and openings along a bedding plane may be enlarged as a result of calcite dissolution by circulating groundwater (Freeze and Cherry, 1979; Fitts, 2002). In our study site, groundwater flowing in the multi-breaking zones of the interbedded layer could not only erode the limestone covering layer, but the mixing of different groundwaters in this layer may also enhance the dissolution of calcite, resulting in gradual and continuous widening of breaking zones. According to Appelo and Postma (2005), there are two modes of groundwater transport through a limestone aquifer, matrix or diffuse flow and conduit flow. Conduit flow, which occurs along larger fissures and openings resulting in enhanced dissolution of carbonate rocks, is the dominant mode of groundwater transport in our study site as suggested by the measured flow rates. Mixing of groundwaters with different compositions will also

produce groundwaters that are undersaturated with calcite, allowing renewed dissolution of carbonate minerals (Alberic and Lepiller, 1998; Batoit *et al.*, 2000). The change in the geochemical properties of groundwater from L-7 and L-11 in the limestone covering layer was most likely caused by the mixing of groundwater from the limestone covering layer and that from the slaty greenstone basement layer.

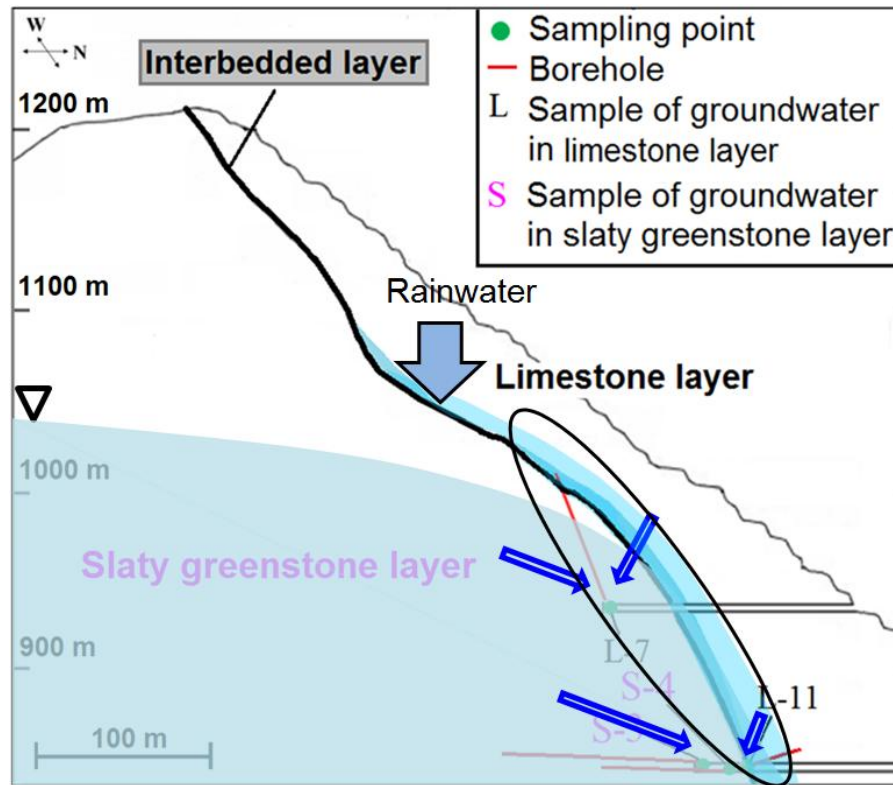


Figure 2.13 Groundwater flow paths (→: blue arrows indicate groundwater of L-7, L-11, S-3 and S-4 that likely originate from mixing between groundwater from the limestone and slaty greenstone layers; ○: circled area indicates the sensitive zones that may affect rock slope)

Based on these results, groundwater flow paths along the interbedded layer are suggested as sensitive zones that may affect the stability of rock slope because it is the most probable region of groundwater mixing (Figure 2.13). In the short term, changes in the groundwater level and flow along the interbedded layer may promote higher pore-water pressure, create higher tensions on cracks and finally generate a potential sliding surface that could ultimately result in a sliding failure along the interbedded layer. Because of the large differences in hydraulic conductivities between these two layers (hydraulic conductivity ratio of the limestone to the slaty greenstone, $4.1 \times 10^{-4} / 4.2 \times 10^{-6} \approx 100$ corresponding to the considerable ratio reported by Dong *et al.*, 2012), groundwater mixed with rainwater may easily infiltrate and percolate through more permeable limestone covering layer but not through the slaty greenstone basement rock. In other words, the slaty greenstone layer with the lower permeability could act as a kind of groundwater barrier and lift the limestone covering layer up. The resultant higher hydraulic head in the limestone covering layer could induce groundwater flow and dissolution of limestone. The higher groundwater flow and more rapid dissolution of limestone grains will affect the bonds between particles and would often reduce

the rock strength by more than 25 % (Záruba and Mencl, 1976). On the other aspect, because the direction of the interbedded layer (45° to 80° dip angle) is sometimes parallel or almost parallel to the slope face (45°–50° slope angle at elevation of 1,000 m upward and 70°–80° at elevation of 1,000 m downward), the pore-water pressure will develop rapidly and provoke the slope failure especially under heavy rainfall as reported by Sharp *et al.* (1972).

2.4 Conclusions

From the chemical analysis and geochemical calculation of groundwater samples collected in the limestone quarry, the findings are summarized as follows:

- (1) The characteristics of groundwater samples were significantly different in each geological formation.
- (2) The hydrochemical facies of all water samples were Ca-HCO₃, formed by calcite dissolution. The changes in quality of several groundwater samples along the interbedded layer may be attributed to the mixing of groundwaters from the limestone covering and slaty greenstone layers. In particular, log $P_{\text{CO}_2(\text{g})}$ and SI_{calcite} of the groundwater noticeably fluctuated on the rainy day.
- (3) Groundwater located along the interbedded layer that may affect the stability of rock slope was suggested by the geochemical survey.

In next parts, results of continuous monitoring of groundwater, geochemical and statistical analyses, groundwater mixing estimation (*e.g.*, by Geochemist's Workbench®), and tritium measurements for dating groundwater were considered to validate the findings of this chapter. At last, recommendations for future work will also be suggested to efficiently extract groundwater in the sensitive zones or design appropriate countermeasures to minimize the effects of these sensitive zones on the stability of the rock slopes based on groundwater geochemistry.

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CHAPTER 3

WATER–ROCK INTERACTION AND CLASSIFICATION OF GROUNDWATERS USING GEOCHEMICAL AND STATISTICAL ANALYSES

3.1 Introduction

In limestone quarries, groundwater chemistry is mainly dominated by the dissolution of calcite, the major mineral component of limestones, because it is moderately soluble in water (Appelo and Postma, 2005). The density, permeability and porosity of limestones primarily depend on the degree of consolidation and development of permeable zones after deposition. Prolonged dissolution may result in enlargement of pore space, which ultimately leads to the development of karst terrain, sinkholes, caves or various features, indicating that the effects of carbonate dissolution on water compositions are quite conspicuous. Consequently, understanding water-rock interaction is critical in evaluating changes in chemical compositions of groundwater along flow paths (Belkhiri *et al.*, 2012). Domenico (1972) and Toth (1984) also mentioned that groundwater chemically evolves by interacting with aquifer minerals and internal mixing among different groundwaters along flow paths. Moreover, variations of groundwater properties may help distinguish groundwater sources and aid in the identification of different geological formations.

The chemical composition of a newly formed groundwater is initially dependent on rainwater (Stumm and Morgan, 1981). As rainwater percolates through soil or sediments, the chemical composition changes especially when fairly soluble carbonate minerals like calcite and dolomite exist in the flow path. For example, the saturation index with respect to calcite is one of the important parameters used to evaluate groundwater flow in many limestone aquifer systems (Peyraube *et al.*, 2014). Because there are many variables involved in the evolution of groundwater, multivariate statistical analyses, in particular the hierarchical cluster analysis (HCA) and principal component analysis (PCA), are often employed to classify, interpret and quantify data on groundwater geochemistry. Love *et al.* (2004), for example, applied PCA to distinguish signatures of uncontaminated groundwater with those impacted by agricultural activities, mining activities and sewage pollution. Similarly, Farnham *et al.* (2003) and Mahlke *et al.* (2003) used PCA to discuss geochemical evolution, mineralization and groundwater contamination in the Ash Meadows-Death Valley of Nevada and central Mexico, USA, respectively. The HCA has also been used to interpret hydrochemical data based on factor scores by Reghunath *et al.* (2002) and Kim *et al.* (2005).

Existence of groundwater in mine sites potentially causes slope stability problems (Zhao *et al.*, 2017). In Japan, for example, there have been several rock slope failures in the limestone quarries partly attributed to groundwater (Yamaguchi and Shimotani, 1986). In recent years, the flow and potentiometric level of groundwater are two of the most important factors affecting the stability of rock slopes (Ulusay *et al.*, 2014; Shen *et al.*, 2017). In this study area, the rock slope was observed to be deformed in response to elevated groundwater levels after intense rainfall events, so groundwater in each geological formation has been monitored and often extracted to lower groundwater levels (Kondo *et al.*, 2016; Ozawa *et al.*, 2016). Their monitored results of crack growths, however, revealed that lowering groundwater at some levels was somehow insufficient to prevent the continued deformation of rock slopes because other factors that had not considered in these previous studies also

affected slope stability. One important parameter related to the instability is the dramatic change in water-rock interaction due to variations in groundwater flow and groundwater mixing in flow paths within three rock strata. Unfortunately, there are few papers that examine the stability of rock slopes in limestone quarries from the geochemical point of view.

The objectives of this chapter are to elucidate the contributions of water-rock interaction to slope stability in the limestone quarry, and to classify groundwater samples and their sources using geochemical and statistical analyses.

3.2 Materials and methods

3.2.1 Site description

The information of the location was the same in Chapter 2, but the water samples surrounding the open-pit limestone quarry were not included in this chapter. However, for understanding each individual chapter, the brief site description was provided (with the updated map showing Japan in full view and its neighboring countries). The limestone quarry is located in the mountainous region of Chichibu city in Saitama prefecture, Japan (Fig. 3.1). The quarry mainly consists of three rock strata: (1) limestone as a covering rock layer, (2) an interbedded layer of limestone and slaty greenstone underlying the covering rock, and (3) slaty greenstone as basement rock (Fig. 3.2(a)). In the covering layer, limestone is mostly grayish to white, microcrystalline and compact. The limestone deposit in this area was formed in the Triassic period (Hayashi *et al.*, 1990) covering the northern half of the mountain, extending 5 km east-westwardly with thicknesses between 500 and 700 m, and lies with a strike of N70°E and dip of 45°–80° north. In the interbedded layer, limestone and slaty greenstone are either interbedded or sometimes mixed in thicknesses of several centimeters to several meters. Limestone and slaty greenstone are both cryptocrystalline while the interbedded layer is characterized by multi-breaking zones. In the basement layer, slaty greenstone has a dark green to red purple color and was formed by alteration of basaltic rocks. Even though the basement slaty greenstone is solid, portions of the rock immediately below the interbedded layer have cracks, joints and weak faces because of structural movements and groundwater flow (Committee on the long-wall rock slope, 2013).

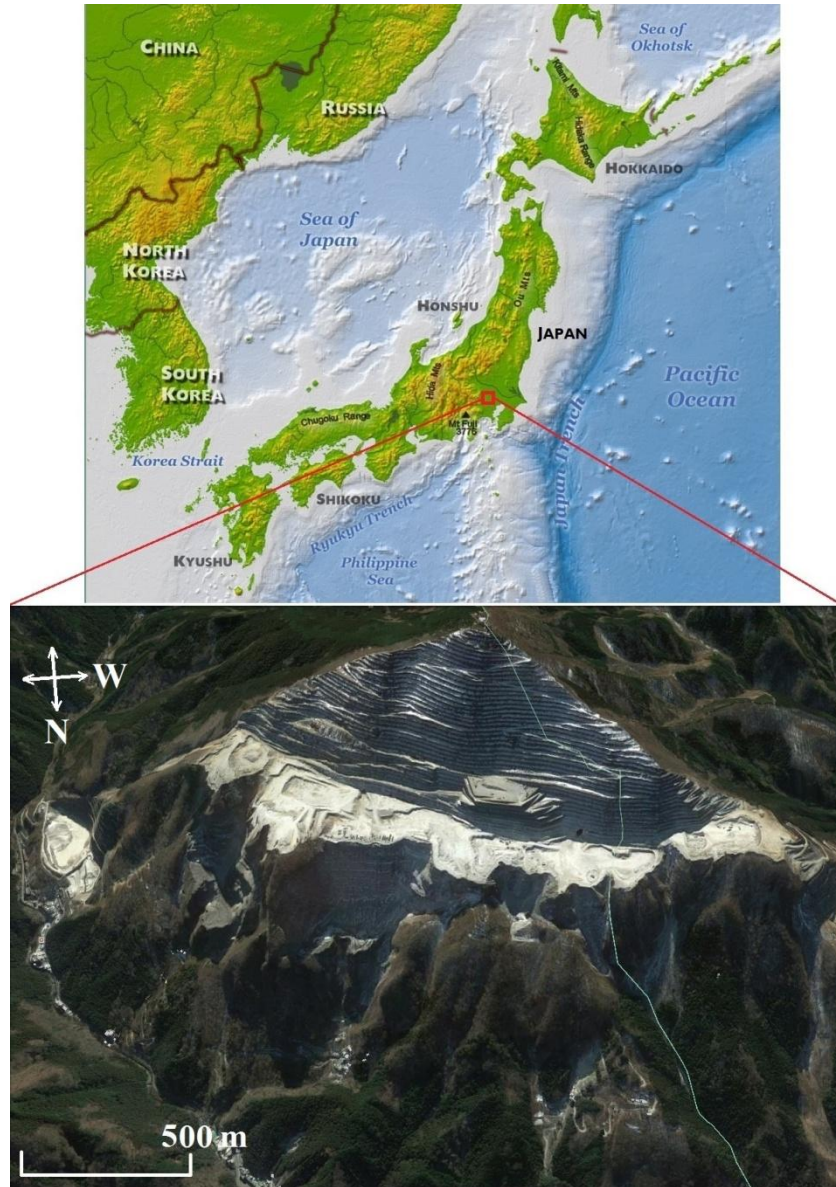


Figure 3.1 Location of the limestone open-pit quarry in Chichibu city, Saitama

3.2.2 Sample collection and analysis procedure

To survey the geological and hydrological conditions inside the quarry, some underground tunnels were excavated. Several boreholes in each tunnel were also drilled upward to drain and monitor groundwater levels. The cross sectional and plan views of the limestone quarry with sampling points are illustrated in Figs. 3.2(a) and 3.2(b). Eleven groundwater sampling campaigns were conducted from December 2014 to November 2016. Thirteen groundwater samples in the limestone layer (L-1–L-11, LP-1 and LP-10) and four in the slaty greenstone layer (S-1–S-4) were collected in each sampling campaign. In total, 160 groundwater samples (121 from the limestone layer and 39 from the slaty greenstone layer) were collected in and around the study area.

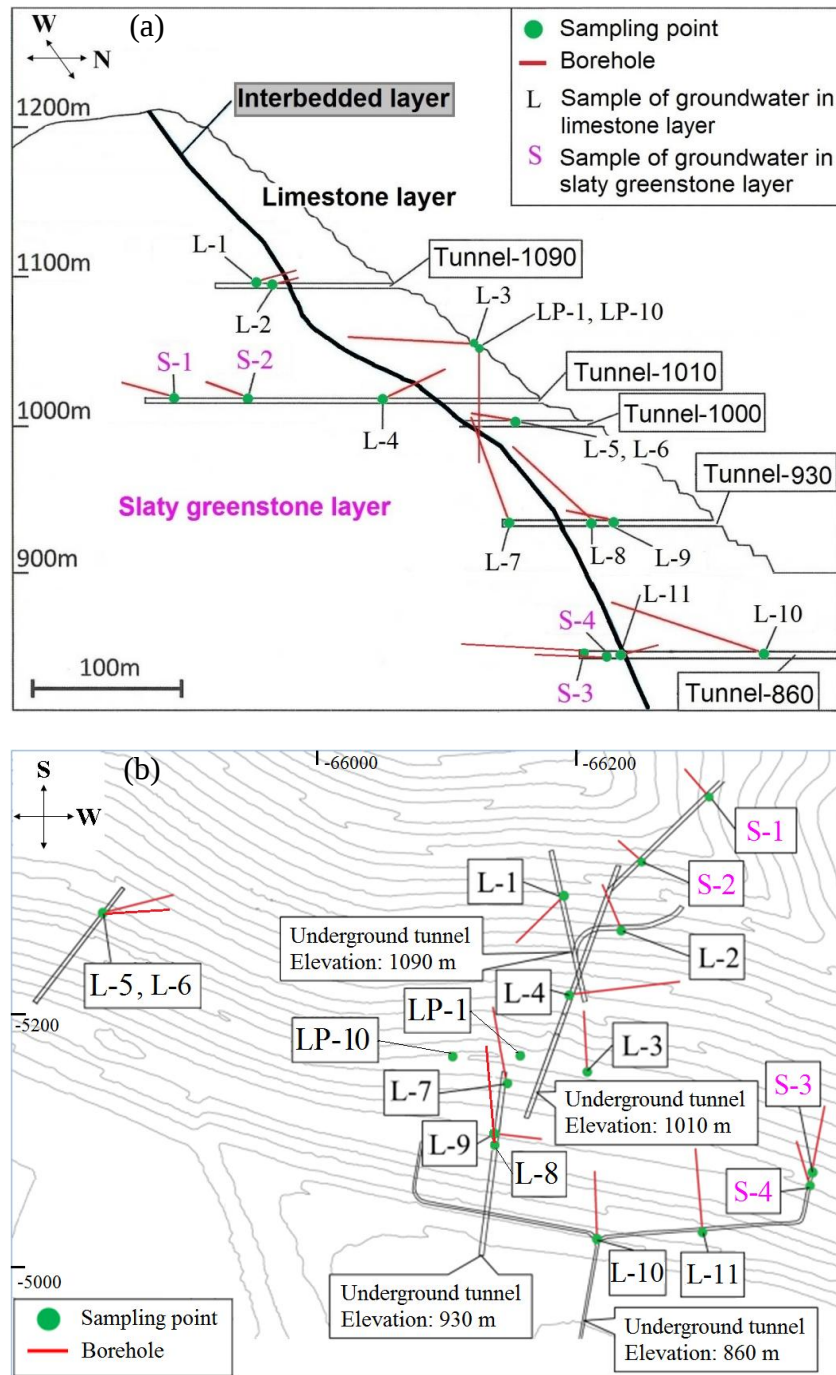


Figure 3.2 Cross sectional view of the limestone quarry (a) and plan view of sampling points of groundwater (b)

Geochemical properties of groundwater were monitored and analyzed periodically. Temperature, pH, oxidation-reduction potential (ORP) and electrical conductivity (EC) of water samples were measured in situ. Their flow rates were also measured by the volumetric method. Groundwater samples were divided into two parts on site in preparation for the chemical analyses. The first one was unfiltered and stored in 250 mL bottles with no air bubble, tightly capping and sealing with plastic tape to avoid degassing or air contact while the second one was filtered through 0.45 μm Millex® membrane filters (Merck Millipore, USA) and stored in 100 mL bottles. The alkalinity was measured by titration with 0.01 M

sulfuric acid in the laboratory immediately after receiving the samples from the quarry. Concentrations of dissolved ions and trace elements were measured using ion chromatographs (ICS-90 and ICS-1000, Dionex Corporation, USA) and an inductively-coupled plasma atomic emission spectrometer (ICP-AES, ICPE-9000, Shimadzu Corporation, Japan), respectively. Ion chromatographs and ICP-AES both have margins of error about 2–3%.

3.2.3 Water-rock interaction

The geochemical evolution of groundwater in the study area is mainly related to changes of Ca^{2+} and HCO_3^- concentrations due to calcite dissolution ($\text{CaCO}_3 + \text{CO}_{2(g)} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$) as described in Chapter 2 and in the previous studies by Eang *et al.* (2016), so the relationship between these two ions was closely monitored. The calculated saturation indices of calcite (SI_{calcite}) by PHREEQC were used to understand water-rock interaction and possible mixing of groundwater in the flow paths.

3.2.4 Multivariate statistical analysis

In hydrogeochemical studies, multivariate statistical analysis is a quantitative and independent approach of groundwater classification (such as grouping groundwater samples and making correlations among the chemical parameters and the samples) and groundwater source identification (Cloutier, 2004). In this paper, two multivariate methods, HCA and PCA, were applied using OriginLab (OriginLab Corp., USA) with the representative dataset of 17 samples from December 2014 to November 2016. The representative dataset here referred to the dataset of each sample from eleven groundwater sampling campaigns by mixing with an equal proportion in volume (*e.g.*, L-1 samples from eleven time collections were mixed together with an equal proportion in volume by Smart Mix function of Geochemist's Workbench to produce the representative L-1 and the same methods for other samples). This representative dataset roughly accounted for the average values, but they may shift a little from the average ones due to the effect of various pH values. Therefore, the dataset became more appropriate especially aiming for mixing of groundwater collected from different periods.

HCA is a data classification technique. Although there are various clustering techniques, HCA is one of the most common methods in earth science and often applied in the classification of hydrogeochemical data (Davis, 1986; Güler *et al.*, 2002). In this study, HCA was carried out with 8 parameters (Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Cl^- , SO_4^{2-} , NO_3^- and HCO_3^-) and the Euclidean distance was utilized as the distance measure or similarity measurement between sampling sites. The sampling sites with the greater similarity are grouped first, and then the steps are repeated until all observations have been classified. Finally, samples were grouped and assigned into the specific clusters under the fixed phenon line. To avoid misclassifications arising from the different orders of magnitude of variables or from the effect of parameters with the highest variances on the calculation of Euclidean distance (Cloutier *et al.*, 2008; Jiang *et al.*, 2015), the variance of each variable was standardized as reported by Davis and Sampson (2002), and meq/L unit was used to well categorize different behaviors of groundwater in the rock layers.

PCA is a data transformation technique and also one of the most widely used multivariate statistical methods in natural sciences, which was developed by Hotelling (1933) from the original work of Pearson. The principal components were computed using the standardized data. The general objective of this technique is to simplify data structure by reducing dimension of the data. In this paper, PCA was applied with 11 parameters of temperature, pH, EC and concentrations of eight major ions. The original parameters would be rearranged into

several new uncorrelated comprehensive components (or factors) without losing significant information (Brown, 1998; Jolliffe, 2002). The calculated components were rotated with the Varimax rotation method, thus creating the loadings of closely related variables in each strengthened component. By the orthogonal projection of the variables on each of the components, the variable loadings were determined. The selected components were based on both the significance (eigenvalue > 1) of the component and the cumulative percentage of explained variance. Finally, the significant step was to interpret each factor in association with the studied issue; however, the main target of this application was to distinguish groundwater samples, and to propose the mixing models to be applied in Chapter 4.

3.3 Results and discussion

3.3.1 Preliminary results of rock properties

The mineral and chemical compositions of representative rock samples, such as limestone in the covering and interbedded layers, and slaty greenstone in the interbedded and basement layers were analyzed by X-ray powder diffraction (XRD) and X-ray fluorescence (XRF), respectively. From the XRD results, limestones in the covering and interbedded layers consist of calcite as their major mineral component. Slaty greenstone in the interbedded layer consists of quartz, albite, calcite, chlorite and hematite while that in the basement layer consists of quartz, albite, chlorite and hematite. From the XRF results, limestone in the covering and interbedded layers contains substantial amounts of CaO with 54.6 and 52.9 wt.%, respectively. Meanwhile, the slaty greenstone contains 38.5 to 39.7 wt.% of SiO₂ as the main chemical component. The details of the mineral and chemical compositions of the different strata were described in Chapter 2.

3.3.2 In situ measurements of groundwater

The results of in situ measurements of groundwater are presented in Fig. 3.3. The flow rates of groundwater in the covering layer ranged from 0.01 to 298 L/min and had larger fluctuations than those of the basement rock ranging from 0.02 to 69.9 L/min (Fig. 3.3(a)) because the hydraulic conductivity of the former (4.1×10^{-6} m/s) was about two orders of magnitude higher than that of the latter (4.2×10^{-8} m/s) (Note: samples LP-1, LP-10 and S-3 were not included in the figure because they were pumped periodically or the flow rates were not measurable). In Fig. 3.3(b), temperatures of groundwater were from 6 to 17.9 °C in the limestone layer and somewhat higher than those in the slaty greenstone layer (8.8-10.5 °C). In Fig. 3.3(c), pH values of groundwater in the limestone layer were from 7.7 to 8.4 and lower than those of groundwater in the slaty greenstone layer (7.8-8.6), which could be attributed to higher partial pressure of CO_{2(g)} in the limestone layer as indicated in Chapter 2. In Fig. 3.3(d), EC values of groundwater in the limestone layer were from 15.9 to 26.5 mS/m and higher than those of groundwater in the slaty greenstone layer (11.1 to 16.9 mS/m), suggesting that total dissolved solids in the limestone layer were higher because of the dissolution of calcite. In Fig. 3.3(e), ORP values of groundwater ranged from 0.075 to 0.25 V in the limestone layer and from 0.10 to 0.21 V in the slaty greenstone layer, indicating that there were no significant differences between the two layers. Also, the groundwater samples were under oxidizing conditions (ORP > 0).

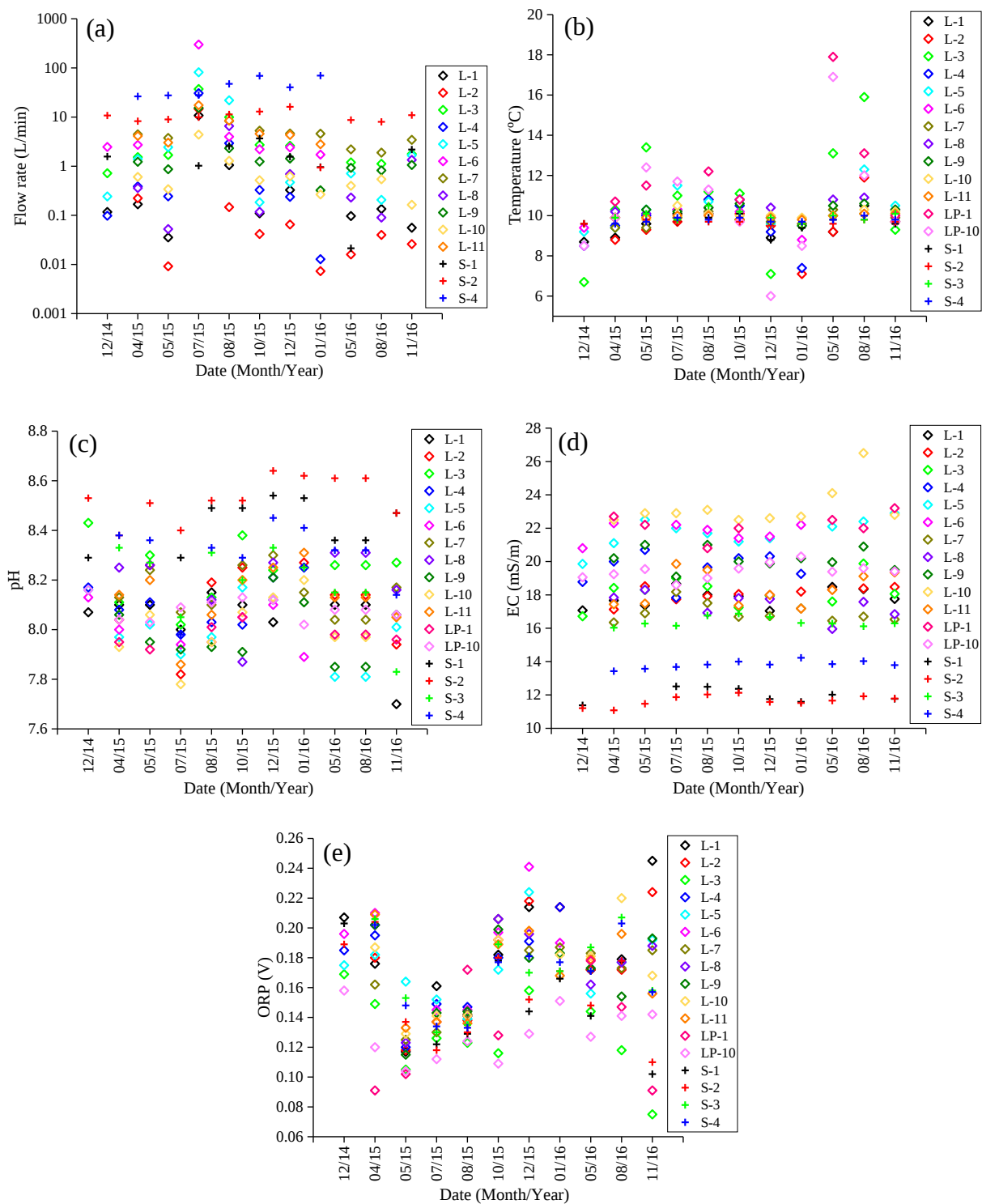


Figure 3.3 Flow rate (a), temperature (b), pH (c), EC (d) and ORP (e) of all groundwater samples collected from December 2014 to November 2016

3.3.3 Water-rock interaction

The relationship between Ca^{2+} and HCO_3^- concentrations is illustrated in Fig. 3.4. The Ca^{2+} and HCO_3^- concentrations of groundwater in the limestone layer were generally higher than those in the slaty greenstone layer. This is to be expected because the limestone has higher

calcite content than the slaty greenstone. In addition, the Ca^{2+} and HCO_3^- concentrations of samples L-7 and L-11 were relatively lower than the other samples from the limestone layer, whereas the Ca^{2+} and HCO_3^- concentrations of samples S-3 and S-4 were fairly higher than those of samples S-1 and S-2 in the slaty greenstone layer. Therefore, groundwaters from L-7, L-11, S-3 and S-4 may originate from the mixing of groundwaters from the limestone and slaty greenstone layers because these sampling points are located near the interbedded layer, which is the boundary layer.

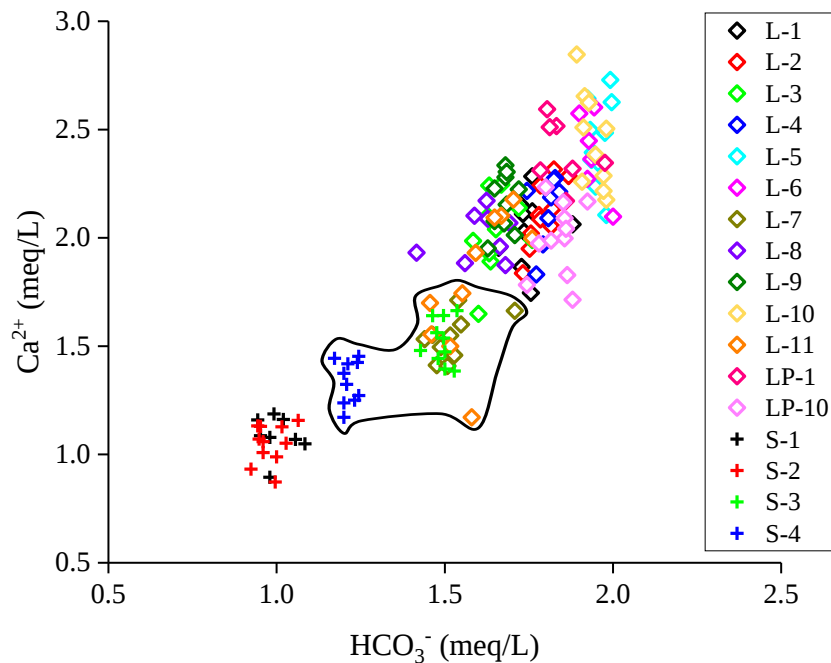


Figure 3.4 Relationship between Ca^{2+} and HCO_3^- concentrations of all groundwater samples (◻: circled area indicates the groundwater samples that may have originated from mixing of groundwaters from the limestone and slaty greenstone layers)

The distribution of SI_{calcite} of groundwater samples is plotted in Fig. 3.5. The SI_{calcite} of groundwater in the limestone layer was mostly larger than zero and also greater than the SI_{calcite} of groundwater in the slaty greenstone layer. The SI_{calcite} decreased in July 2015, which suggests that the recharge of rainwater could correspond to young groundwater in term of residence time (Reilly *et al.*, 1994; Clark and Fritz, 1997). This means that the groundwater mixed with rainwater may not have sufficient time to equilibrate with calcite owing to the faster flow rate. Merkel and Planer-Friedrich (2008) pointed out that the SI range of 0 ± 0.05 was supposed to be in equilibrium due to inherent uncertainties in calculation of SI s such as the accuracy of chemical analysis, mineral equilibrium constant and the method of calculating ion activities. This means that most of the groundwater samples from the limestone layer were supersaturated or in equilibrium with calcite except those collected in July 2015. The groundwater samples in the slaty greenstone layer were dominantly in equilibrium or undersaturated with calcite. From Wigley and Plummer (1976) and Batoit *et al.* (2000), mixing of two groundwaters with different compositions can lead to undersaturation of calcite in the resulting groundwater leading to the renewed dissolution of calcite in carbonate aquifers, even if the two original groundwaters are in equilibrium before mixing. Also, the

general compositions of mixed groundwater would lie somewhere between the compositions of the original groundwaters. Therefore, the change in quality of groundwater samples L-7, L-11, S-3 and S-4 was most likely caused by mixing groundwater from the limestone covering layer and slaty greenstone basement layers. On the rainy day, the mixing was also affected by rainwater infiltrating through the limestone covering layer.

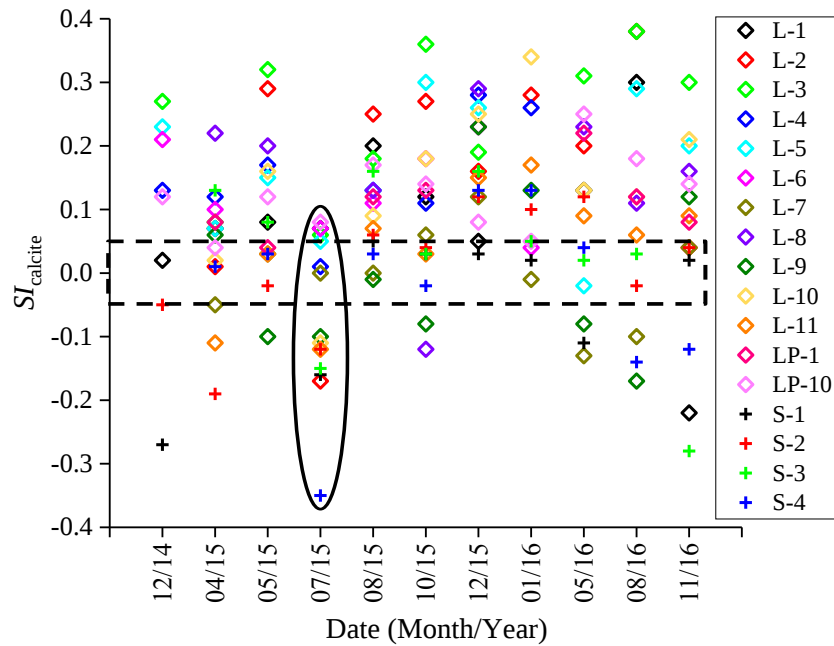


Figure 3.5 SI_{calcite} of all groundwater samples (---: dashed rectangle indicates the saturated condition of calcite mineral; 0: circled area indicates the rainy days)

3.3.4 Multivariate statistical analysis

3.3.4 (a) Hierarchical cluster analysis

As part of HCA results, the descriptive statistics are given in Table 3.1 to summarize the characteristics and variation between clustering variables, whereas the procedure of cluster stages, statistically grouping from the smallest to the highest distances, is presented in Table 3.2.

Table 3.1 Descriptive statistics of the concentrations (meq/L) of 8 major ions

Parameters	<i>N</i>	Mean	<i>SD</i>	Sum	Min	Median	Max
Na ⁺	17	0.067	0.026	1.147	0.031	0.075	0.119
Mg ²⁺	17	0.131	0.094	2.235	0.031	0.087	0.310
K ⁺	17	0.006	0.002	0.109	0.003	0.006	0.011
Ca ²⁺	17	1.911	0.454	32.49	1.048	2.021	2.446
Cl ⁻	17	0.029	0.007	0.489	0.019	0.028	0.050
SO ₄ ²⁻	17	0.184	0.100	3.120	0.068	0.169	0.382
NO ₃ ⁻	17	0.037	0.032	0.631	0.013	0.021	0.097
HCO ₃ ⁻	17	1.653	0.320	28.10	0.978	1.720	2.003

※*SD*: standard deviation and *N*: number of representative samples

Table 3.2 Cluster stages of statistical grouping

Stage	Distance	Cluster 1	Cluster 2	Number of clusters	New cluster	Next stage
1	0.045	14	15	16	14	13
2	0.048	3	8	15	3	9
3	0.056	5	6	14	5	8
4	0.057	1	2	13	1	7
5	0.127	10	12	12	10	8
6	0.133	7	16	11	7	12
7	0.145	1	4	10	1	9
8	0.170	5	10	9	5	14
9	0.202	1	3	8	1	10
10	0.230	1	13	7	1	11
11	0.239	1	9	6	1	14
12	0.330	7	11	5	7	15
13	0.360	14	17	4	14	15
14	0.457	1	5	3	1	16
15	0.692	7	14	2	7	16
16	1.004	1	7	1	1	

To quantify the similarity of the samples, HCA was then performed based on the concentrations of major ions in groundwater, and the dendrogram of HCA is presented in Fig. 3.6. The phenon line determined the number of clusters by mainly considering the significant variation of Ca^{2+} - HCO_3^- distributions. As a result, the phenon line was defined as the distance of 0.6, by which all samples were classified into three statistically significant clusters (which represented the similarity of the individual samples). Cluster I was composed of the groundwater samples mainly located in the limestone layer with larger similarity (*e.g.*, higher concentrations of Ca^{2+} and HCO_3^-) and stable quality. These groundwaters were regarded as an original groundwater from the covering layer. Most samples in Cluster II were located along the interbedded layer, where the groundwaters were possibly mixed between groundwaters from the limestone and slaty greenstone layers. However, groundwater sample S-4 was not in this cluster because it was not dramatically mixed with groundwater from the limestone layer. Cluster III basically consisted of groundwaters from the basement slaty greenstone layer. Groundwaters from S-1 and S-2 had similar and stable quality, for example, lower concentrations of Ca^{2+} and HCO_3^- . In consequence, these two groundwaters were assumed to be the original groundwater from the basement slaty greenstone layer.

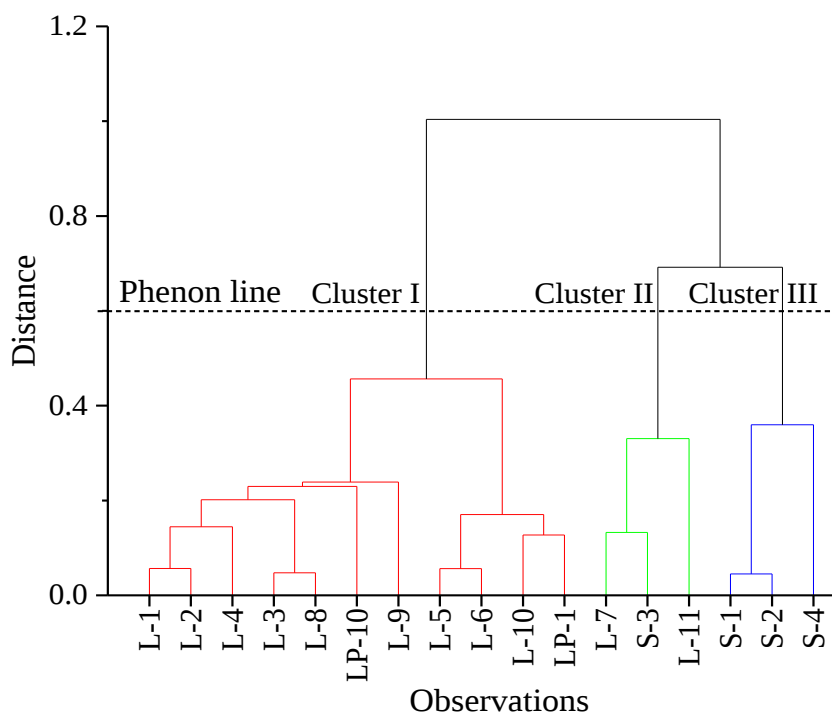


Figure 3.6 Dendrogram from the HCA for all groundwater samples

3.3.4 (b) Principal component analysis

As part of PCA results, the symmetrical correlation matrix was computed as shown in Table 3.3. The results showed that EC, Ca^{2+} and HCO_3^- were in positively strong correlations with each other (with correlation coefficients $R > 0.9$) due to calcite dissolution and next followed by Mg^{2+} and Na^+ (with $R = 0.86$), which may result from the dissolved ionic compounds of Mg and Na-bearing minerals. On the other hand, EC, Ca^{2+} and HCO_3^- were in negatively strong correlations with pH (with $R < -0.9$), simply explained that the solubility of CaCO_3 increased with a decrease in pH (*e.g.*, the lower pH induced the higher dissolution of CaCO_3).

Table 3.3 Correlation matrix of temperature ($^{\circ}\text{C}$), pH, EC (mS/m) and concentrations (meq/L) of 8 major ions

Parameters	Temp.	pH	EC	Na^+	Mg^{2+}	K^+	Ca^{2+}	Cl^-	SO_4^{2-}	NO_3^-	HCO_3^-
Temp.	1										
pH	-0.346	1									
EC	0.447	-0.944	1								
Na^+	0.075	0.182	-0.256	1							
Mg^{2+}	-0.200	0.511	-0.589	0.863	1						
K^+	0.080	-0.058	-0.020	0.546	0.467	1					
Ca^{2+}	0.409	-0.902	0.971	-0.460	-0.758	-0.156	1				
Cl^-	0.203	0.370	-0.242	0.043	0.027	-0.158	-0.205	1			
SO_4^{2-}	0.547	-0.702	0.771	0.179	-0.223	0.011	0.667	-0.054	1		
NO_3^-	-0.278	0.754	-0.762	0.457	0.640	-0.118	-0.789	0.320	-0.400	1	
HCO_3^-	0.324	-0.926	0.966	-0.391	-0.635	-0.015	0.964	-0.345	0.596	-0.83	1

※Values in bold number indicate the very significant correlations; Temp.: temperature

Parameters	Coefficients of PC1	Coefficients of PC2	Coefficients of PC3
Temp.	0.178	0.246	0.529
pH	-0.380	-0.164	0.104
EC	0.399	0.125	0.034
Na ⁺	-0.184	0.587	0.057
Mg ²⁺	-0.305	0.418	-0.085
K ⁺	-0.045	0.507	-0.283
Ca ²⁺	0.407	-0.026	0.046
Cl ⁻	-0.114	-0.095	0.690
SO ₄ ²⁻	0.278	0.332	0.291
NO ₃ ⁻	-0.349	0.014	0.202
HCO ₃ ⁻	0.398	0.039	-0.118
Eigenvalue	5.90	2.11	1.38
Explained variance	53.63%	19.19%	12.56%
Cumulative variance	53.63%	72.82%	85.38%

※ Values in bold number indicate the relatively significant loading and contribution to the responding components

The rotated factor loadings of principal components on variables and the biplot from PCA are illustrated in Table 3.4 and Fig. 3.7, respectively. Three major principal components (PC1, PC2, and PC3) affecting the quality of groundwater are identified, which accounted for 85.4% as the cumulative variance of the original data structure (Table 3.4). The data shown in bold in Table 3.4 indicate the relatively significant loading and contribution to the responding components. PC1, which explained 53.6% of the total variance, had strong loadings on pH, EC, Ca²⁺, NO₃⁻ and HCO₃⁻. The pH and NO₃⁻ both had the negative coefficients to this factor and they were positively correlated with each other, whereas the EC and the major ions (Ca²⁺ and HCO₃⁻) had the positive coefficients governed by water-rock interaction in the flow path. PC2 accounted for 19.2% of the total variance, which was positively correlated with Na⁺, Mg²⁺, K⁺ and SO₄²⁻, probably indicating the impact of Na, Mg and K-bearing minerals in association with SO₄ on groundwater or the impact of silicate minerals containing Na, Mg and K since Si was fairly correlated with Na ($R = 0.7$), Ma ($R = 0.9$) and K ($R = 0.3$) (see Supplementary Table 1 in Appendix B). Lastly, PC3 corresponding to 12.6% of the total variance, was affected by temperature and Cl⁻. These may be attributed to background or outer factors like atmospheric temperature and rainwater, while Cl⁻ concentrations of the groundwater were approximate to that of the rainwater (0.02 meq/L, see Supplementary Table 2 in Appendix B). Since PC1 and PC2 governed the majority of the loadings, PC1 and PC2 were considered in the biplot (combination of loadings and scores) from PCA (Fig. 3.7). The plots show the characteristics of the components and help to clearly understand the relative importance of variables in components. The samples in Cluster I were plotted along the positive side of PC1, indicating that their geochemistry is mainly controlled by calcite dissolution. These samples statistically corresponded to the original groundwater in the covering limestone layer. The samples in Cluster II were plotted in negative and positive directions of PC1 and PC2, respectively, and interpreted as the mixed groundwater between the groundwater from the limestone layer or rainwater flowing through the limestone layer and groundwater from the slaty greenstone layer. The samples in Cluster III were plotted in negative directions of PC1 and PC2. However, groundwater sample S-4 was slightly shifted to the upper zone close to Cluster II, indicating that this groundwater is somewhat mixed

between the groundwater from the covering limestone and basement slaty greenstone layers, while groundwaters from S-1 and S-2 statistically regarded as the original groundwater in the basement layer.

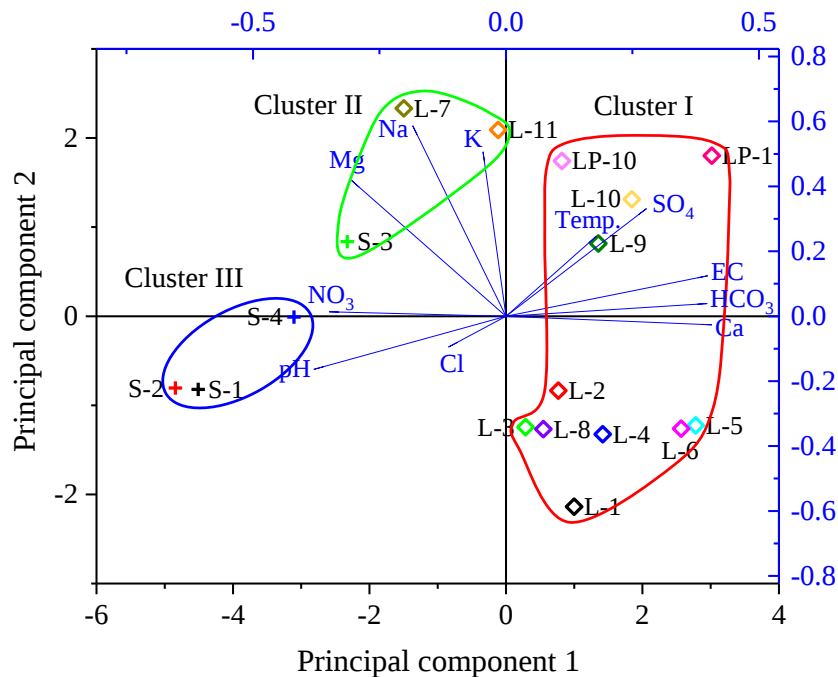


Figure 3.7 Biplot from the PCA for all groundwater samples

3.4 Conclusions

By using the monitored groundwater geochemistry from a limestone quarry and analyses of the data by PHREEQC, HCA and PCA, the findings in this chapter are summarized as follows:

- (1) Water-rock interaction within the quarry was distinguished by individual layers, all of which geochemically evolved as a function of calcite dissolution.
- (2) The groundwater samples were classified into the original groundwater from the limestone layer, the mixed groundwater along the interbedded layer, and the original groundwater from the slaty greenstone layer.
- (3) The above results suggest the necessity of continuous monitoring of groundwater.

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CHAPTER 4

MIXING ESTIMATION, DATING OF GROUNDWATER AND IDENTIFYING ZONES AFFECTING THE ROCK SLOPES

4.1 Introduction

4.1.1 Groundwater mixing overview

Estimation of groundwater mixing ratios is a crucial task in groundwater management, for example, the estimation of river infiltration (Edmunds *et al.*, 1992; Beyerle *et al.*, 1999; Farah *et al.*, 2000), intrusion from leaky aquifers or brines (Balderer *et al.*, 1996; Cook and Herczeg, 2000) and other specific purposes. The quantity as well as quality of groundwater resources is sensitive to, *e.g.*, the admixture river water, interaction between different groundwater layers and spatial distribution of such mixing zones. Mixing ratios of different groundwater components can be calculated if the mixed waters have distinct signatures, *e.g.*, different chemical and/or isotopic evolution (Rueedi *et al.*, 2005). In addition, the composition of end members in larger aquifers may vary considerably due to water-rock interaction or varying recharge conditions. After selecting sampling sites where no mixing occurs, the spatial distribution of the end member composition could be calculated using interpolation method, for example, Kriging (Rueedi *et al.*, 2005).

With respect to hydrochemical differences in the London Basin, Ineson and Downing (1963) considered mixing of groundwaters as one possible mechanism responsible for many of the chemical differences in the confined section, while Downing and Williams (1969) figured out that dilution attributed the major changes to ionic replacement in the Lincolnshire limestone. Cederstom (1946) discussed the occurrence of mixing in sand aquifers of the coastal plains in Virginia and the different hydrochemical facies of groundwaters beneath the hydraulic gradient, although the real extent of differences in the hydrochemical facies' distribution depends on the type of aquifer, particularly in an "interface zone". However, Lawrence *et al.* (1976) mentioned that mixing and related chemical changes were not demonstrated in detail by the above authors. They explained that the hydrochemistry and mixing of different groundwater types occurred between modern recharge water and ancient-possibly-connate water in the "interface zone", where the relationship of sulfate reduction and bicarbonate in younger water was considered to be related indirectly to mixing.

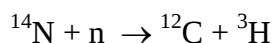
Many aspects of mixing are linear (*e.g.*, the variation of total species concentrations), while some aspects like the ion activity product are non-linear. Also, this non-linearity is particularly significant in determining mineral saturation levels (Wigley and Plummer, 1976). The mixing of solutions of different chemical compositions is known to produce the mixture in which the molalities and activities of individual ions are often non-linear functions of their end-member values, especially for solutions containing dissolved carbonate species (Wigley and Plummer, 1976). Runnells (1969) has shown that mixing of two solutions which are both undersaturated with respect to a given mineral may lead to a mixture which is either supersaturated or more strongly undersaturated depending on the chemical character of the original solutions and on the mineral in question. Similarly, mixing of two carbonate groundwaters which are both saturated with respect to calcite can lead to undersaturated conditions if the original groundwaters have either different P_{CO_2} (Bögli, 1964) or different temperatures (Thraillkill, 1968). For waters of widely differing chemical compositions, the

opposite effect (*i.e.*, a supersaturated mixture) may also occur (Wigley, 1973). These aspects of mixing are of considerable importance in explaining diagenetic processes in carbonate sediments and rocks (Matthews, 1971; Badiozamani, 1973; Wigley, 1973; Plummer, 1975; Plummer *et al.*, 1976). Non-linear behaviour can be attributed to some important factors such as the algebraic effects, ΔP_{CO_2} effect, and ionic strength effect. In investigating mixing problems in natural environments, it is convenient to consider two idealized systems, which are either closed or open to CO_2 gas. If mixing occurs under closed system conditions, the total molality of inorganic carbon in the mixture is determined from the total carbonate of the end-member solutions, and P_{CO_2} is a function of the composition of the mixture. In systems open to CO_2 , *i.e.*, in the presence of an infinite reservoir of CO_2 gas, the total carbonate is not conserved and the mixture P_{CO_2} is determined by the P_{CO_2} of the environment (Wigley and Plummer, 1976).

4.1.2 Tritium fundamentals

Tritium (^3H), a naturally occurring radioactive isotope of hydrogen, has a mass number of 3. It has one proton and two neutrons and is a soft beta emitter (Cook and Solomon, 1997). It emits low-energy beta particle and has a maximum energy of 0.018 MeV (million electron volts). The discovery of tritium is attributed to Ernest Rutherford and his co-workers at the Cavendish Laboratory in England (Hoffman and Stewart, 1966).

The occurrence of tritium in waters of the hydrological cycle arises from both natural and man-made sources (Freeze and Cherry, 1979) and is found naturally in both air and water. Tritium is most useful for distinguishing between pre-bomb and post-bomb recharge (Cook and Solomon, 1995). Tritium is naturally produced in the atmosphere by cosmogenic processes and interacts with atmospheric nitrogen and oxygen. Atmospheric tritium is formed when cosmic rays hit nitrogen to yield ^3H , and this occurs according to the following reaction:



where n is a neutron from cosmic radiation. Tritium atoms then combine with oxygen, forming water that subsequently falls as precipitation. Small amounts of natural tritium are also produced by alpha decay of lithium-7 in the earth (Schlosser *et al.*, 1988).

Beginning in 1953, tritium concentrations in the atmosphere and consequently in precipitation began to increase because of nuclear weapon tests. The large-scale nuclear weapon testing during the early 1960s resulted in tritium concentrations up to 3 orders of magnitude greater than natural conditions (Reilly *et al.*, 1994).

4.1.3 Tritium as an indicator of groundwater age

Groundwater age is generally considered as the average travel time for a water parcel from either the surface or the water table (point of recharge) to a given point in the aquifer. Groundwater dating (age estimation) is the estimation of the groundwater age by one or more available techniques. The term “residence time” is here used synonymously with “age”. Hence, the residence time of groundwater is here defined as the average travel time between the point of recharge and the point of discharge, *e.g.*, to a river, lake or any monitoring point in the groundwater zone. In addition, there are basically three different ways of estimating groundwater age at a groundwater well or monitoring point: (1) by environmental tracers (*e.g.*, Plummer *et al.*, 1993), (2) by groundwater flow modelling (Engesgaard and Molson, 1998) and (3) by a combination of both (Bauer *et al.*, 2001; Trolborg, 2004).

By the analysis of environmental tracers (*e.g.*, ^3H , CFCs, SF_6 , ^{85}Kr , ^{36}Cl , ^{14}C , etc.) in groundwater, direct information about groundwater age, flow paths, flow velocities,

contaminant transport mechanisms etc. can be obtained. Particularly, tritium is one of the most common environmental tracers used for obtaining time scales for the physical mixing and movement of groundwater. The tritium atom, substituting for the hydrogen atom in the water molecule, follows the path of water through the groundwater flow system (Reilly *et al.*, 1994). On the other hand, because tritium has a half-life of 12.43 years (Unterweger *et al.*, 1980), it may suit for groundwaters younger than 1950s and dating young groundwater is common to distinguish between young (modern) groundwater and old (submodern) groundwater. Young groundwater is considered to be groundwater with a human impact recharged since about 1950s, while old groundwater recharged the aquifers before 1950s generally does not exhibit any significant human impact, *i.e.*, pre-nuclear detonation waters (Plummer *et al.*, 1993; Cook and Herczeg, 2000; Hinsby *et al.*, 2001).

Additionally, research during the past decade has introduced tritium as a significant tracer being applied in an increasing number of studies for recognition of modern water components, possibly containing contaminants, and for groundwater dating (Hinsby *et al.*, 2001; Manning *et al.*, 2005; Hinsby *et al.*, 2007). The other authors reported that the application of tritium (^3H) together with its daughter nuclide ^3He can be used for estimating absolute groundwater ages (Solomon and Cook, 2000; Manning *et al.*, 2005).

In Chapter 3, a combination of geochemical analysis dealing with water-rock interaction and statistical methods was presented, which involved all measured parameters in the investigated area to identify original groundwater sources and mixing zones. However, mixing ratios of groundwaters had not been estimated yet between the original groundwaters from the limestone covering and slaty greenstone basement layers, and the groundwater ages/residence times were unknown either.

Therefore, the objectives of this chapter are to estimate and verify possible mixing of groundwaters within the rock layers using geochemical models, to define groundwater ages by tritium analysis, and to clarify sensitive zones affecting rock slopes for efficient groundwater abstraction in the sensitive zones and for improvement of the stability of rock slopes.

4.2 Materials and methods

4.2.1 Sampling points

For groundwater mixing evaluation, the number of samples and sampling points were the same as in Chapter 3, meaning that eleven groundwater sampling campaigns were conducted from December 2014 to November 2016. Thirteen groundwater samples in the limestone layer (L-1–L-11, LP-1 and LP-10) and four in the slaty greenstone layer (S-1–S-4) were collected in each sampling campaign. In total, 160 groundwater samples (121 from the limestone layer and 39 from the slaty greenstone layer) were collected in and around the study area. The sampling points were demonstrated in Figure 4.1 (and the details of sampling method were provided in Chapter 3).

However, for tritium analysis only four groundwater samples from the limestone quarry (*i.e.*, three in the limestone covering layer: L-2, L-7 and LP-10; and one in the slaty greenstone basement layer: S-2) and one shallow groundwater (SW-1) from the spring nearby the quarry, in Figure 4.1, were collected as the first trial. A snow sample in the study area was also collected. These samples were collected on August 15–16, 2016 except the snow sample that was collected on March 01, 2017. One liter of each unfiltered (original) groundwater sample was taken into a plastic bottle and dispatched to Japan Environment Research Co., Ltd. in Yoshikawa city of Saitama. This trial was expected to obtain some significant results for further tritium analysis of groundwater in this study area.

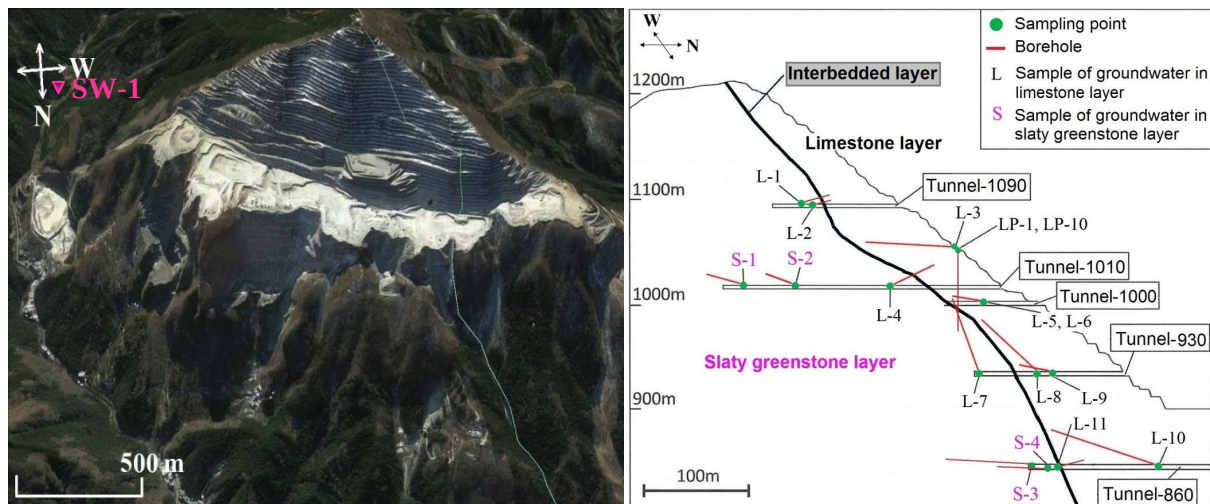


Figure 4.1 Sampling points

4.2.2 Groundwater mixing estimation

4.2.2 (a) Mixing estimation using Ca^{2+} and HCO_3^- concentrations

Mixing between groundwaters from the limestone covering and the slaty greenstone basement layers evidently occurred where the boundary layer is thinning out. The variations of Ca^{2+} and HCO_3^- concentrations were key indicators because calcite dissolution within groundwater flow paths played an important role. The concentrations of other ions were very low, almost constant and apparently independent of the geological formation in this study. Therefore, Ca^{2+} and HCO_3^- concentrations of groundwater, which differ significantly between the limestone covering and the slaty greenstone basement layers, were used as parameters to estimate the mixing fractions. The relationship between Ca^{2+} and HCO_3^- concentrations would conform to a linear regression line, which represents the mixing fraction line. By comparing the distance on the line of mixing fraction between the original and the mixed groundwaters, the mixing fractions could be estimated with manual calculations.

4.2.2 (b) Mixing estimation using Flash Diagram

Using the Flash Diagram function in Geochemist's Workbench® version 11 (GWB, Aqueous Solutions LLC), mixing fractions of the groundwaters formed by mixing between groundwaters from the limestone covering and the slaty greenstone basement layers were also determined to crosscheck the mixing results from section 4.2.2 (a). Most of the geochemical data (e.g., pH, temperature, concentrations of ions and elements) were used as the input parameters. Mixing fractions between groundwaters from the two layers in respect with Ca^{2+} concentrations were considered in the plot from Flash Diagram (see more descriptions in 4.3.1 (b)). The mixing fractions of mixed groundwater were derived from the plot relying on the Ca^{2+} concentrations. If the mixing results from the above section tend to be the same or similar to those results from this section, all the obtained mixing ratios could be reliable and validated. With regard to groundwater flow paths and mixing conditions, sensitive zones affecting the stability of rock slopes would be ultimately identified.

4.2.3 Tritium measurements

If tritium is present in sufficient amounts, the tritium concentration may be determined directly by use of a liquid scintillation spectrometer. An aliquot of water sample is mixed with a scintillator solution in a polyethylene vial and placed between two photomultiplier tubes in the spectrometer. As the tritium decays, the emitted beta particles excite the scintillator solution generating light pulses that are detected and amplified by the photomultiplier tubes and electronically sorted according to pulse energy into the appropriate sealer channel (Bell and Hayes, 1958). The window on the analyzer channel is adjusted to accept the major part of the tritium spectrum by excluding excessive background noise and the higher part of the energy spectrum.

Although tritium is typically measured by liquid scintillation counter of the decay events (Motzer, 2007), the low tritium activity of environmental samples generally requires that the water samples are electrolytically enriched to lower the detection limit. This allows an order of magnitude greater detection limit (*i.e.*, < 0.1 TU according to Freeze and Cherry, 1979) than by direct counting of water. Samples are mixed with scintillation cocktail and decay-counted in a low-background Quantulus liquid scintillation counter. In this research work, the methodology of tritium analysis was conducted following the procedure described in Tritium Analysis Method - Radioactivity Measurement Series 9 (Ministry of Education, 1996). Measuring device is liquid scintillation counter, namely liquid scintillation analyzer model 3100 TR (PerkinElmer, Inc., USA). From this analysis, the tritium concentration are typically given in both units, TU (standing for tritium unit where $1 \text{ TU} = 1$ tritium atom per 10^{18} hydrogen atoms) and Bq/L (standing for Becquerel per litter where $1 \text{ Bq} = 1$ decay event per second and $1 \text{ TU} = 0.118 \text{ Bq/L}$).

4.3 Results and discussion

4.3.1 Groundwater mixing estimation

Based on the results of Chapter 2, the statistical analyses (*i.e.*, HCA and PCA) including the distributions of water-rock interaction in Chapter 3, and/or the findings suggested by Eang *et al.* (2017a; 2017b), concepts of groundwater mixing are divided into two cases as follows:

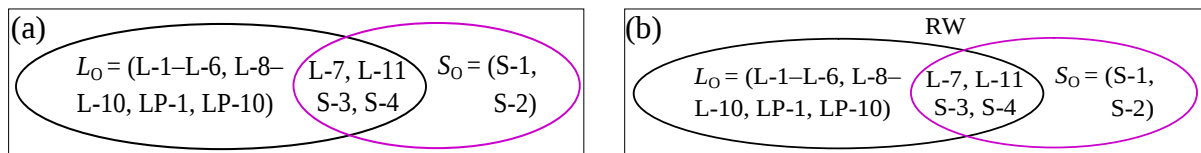


Figure 4.2 Concepts of groundwater mixing for normal days (L_O and S_O : original groundwater from the limestone and slaty greenstone layers, respectively; L-7, L-11, S-3 and S-4: groundwater formed by mixing) (a) and for rainy days (L_O and S_O : original groundwater from the limestone and slaty greenstone layers, respectively; RW: rainwater) (b)

Concept of groundwater mixing for the case of normal days (*i.e.*, all sampling periods except July 2015) is presented in Fig. 4.2(a). Groundwaters from L-7, L-11, S-3 and S-4 were assumed to be mixtures of original groundwater from the limestone (L_O) and slaty greenstone layers (S_O). Note that every sample was in general from ten time collections for the case of normal days. Thus, the representative of individual samples was basically carried out in the

concept of mixing (*e.g.*, L-1 samples from ten time collections were mixed together with an equal proportion in volume by GWB's Smart Mix function to produce the representative L-1 and the same methods for other samples, see the detailed explanation in section 3.2.4 of Chapter 3). L_O was obtained by mixing equal proportions in terms of volume of samples L-1–L-6, L-8–L-10, LP-1 and LP-10 (by GWB's Smart Mix function) on the normal days, while S_O was obtained by mixing equal proportions in volume of samples S-1 and S-2, following the same method as L_O in this case.

Concept of groundwater mixing for the case of rainy days (*i.e.*, the sampling period on July 2015) is provided in Fig. 4.2(b). Groundwaters from L-7, L-11, S-3 and S-4 were the mixture of original groundwaters from the limestone (L_O) and slaty greenstone layers (S_O) that were affected by rainwater (RW). L_O was obtained by mixing with equal proportions in volume of samples L-1–L-6, L-8–L-10, LP-1 and LP-10 (by GWB's Smart Mix function) on the rainy days, while S_O was obtained by mixing equal proportions in volume of samples S-1 and S-2, following the same method as L_O for the rainy days.

4.3.1 (a) Mixing estimation using Ca^{2+} and HCO_3^- concentrations

By plotting Ca^{2+} and HCO_3^- concentrations of L_O , L-7, L-11, S-3, S-4 and S_O , estimation of the mixing fractions for normal and rainy days is detailed as follows:

(1) Case of normal days – all sampling periods except July 2015 (Fig. 4.3):

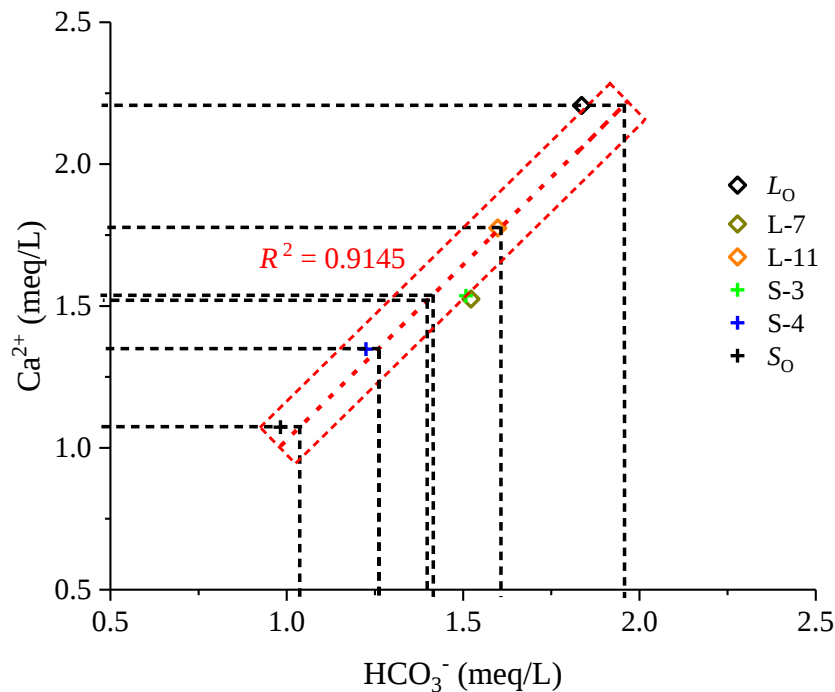


Figure 4.3 Mixing estimation using Ca^{2+} and HCO_3^- concentrations for normal days

The relationship between Ca^{2+} and HCO_3^- concentrations of L_O , L-7, L-11, S-3, S-4 and S_O for the normal days is illustrated in Fig. 4.3. The red-dashed rectangle is the extrapolation of red-dashed line that represents the linear regression (with determination coefficient $R^2 = 0.91$) and the line of mixing fraction. From this figure, the coordinate projections of HCO_3^- and Ca^{2+} concentrations of L_O , L-7, L-11, S-3, S-4 and S_O corresponded to (1.96, 2.20), (1.40,

1.52), (1.61, 1.78), (1.42, 1.54), (1.27, 1.35) and (1.03, 1.08), respectively. By comparing the distances from L-7 to L_O , L-11 to L_O , S-3 to L_O and S-4 to L_O with the distance from S_O to L_O , the mixing fractions of L-7, L-11, S-3 and S-4 were derived as follows: 39% L_O :61% S_O , 62% L_O :38% S_O , 41% L_O :59% S_O and 25% L_O :75% S_O .

(2) Case of rainy days – sampling period on July 2015 (Fig. 4.4):

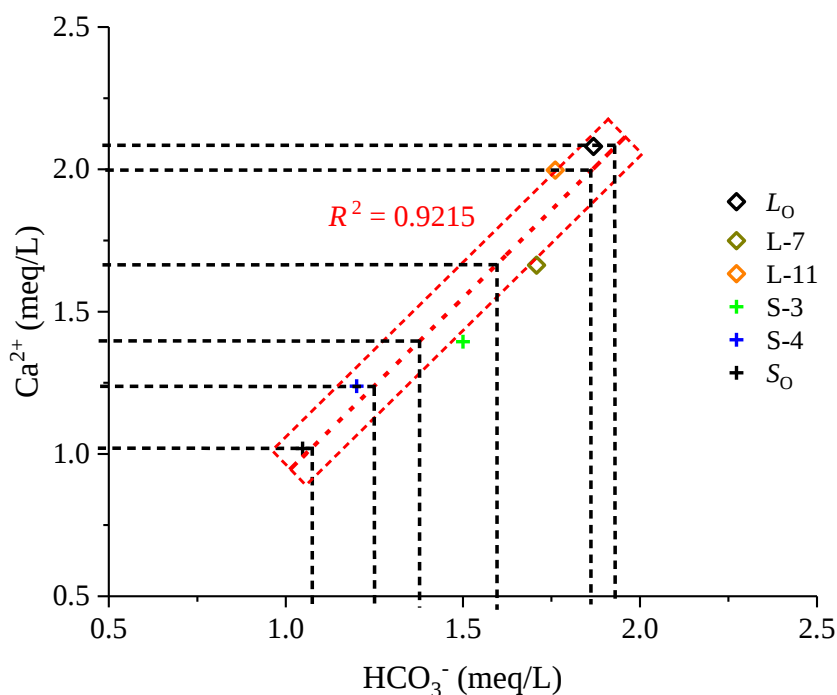


Figure 4.4 Mixing estimation using Ca^{2+} and HCO_3^- concentrations for rainy days

The relationship between Ca^{2+} and HCO_3^- concentrations of L_O , L-7, L-11, S-3, S-4 and S_O for rainy days is demonstrated in Fig. 4.4. The red-dashed rectangle is the extrapolation of red-dashed line that represents the linear regression (with determination coefficient $R^2 = 0.92$) and the line of mixing fraction. From this figure, the coordinate projections of HCO_3^- and Ca^{2+} concentrations of L_O , L-7, L-11, S-3, S-4 and S_O corresponded to (1.93, 2.09), (1.59, 1.66), (1.87, 2.0), (1.38, 1.40), (1.25, 1.24) and (1.08, 1.02), respectively. By comparing the distances from L-7 to L_O , L-11 to L_O , S-3 to L_O and S-4 to L_O with the distance from S_O to L_O , the mixing fractions of L-7, L-11, S-3 and S-4 were derived as follows: 60% L_O :40% S_O , 92% L_O :8% S_O , 35% L_O :65% S_O and 20% L_O :80% S_O .

4.3.1 (b) Mixing estimation using Flash Diagram

By considering the geochemical data, the mixing results using the Flash Diagram for the both cases of normal days and rainy days are provided as follows:

(1) Case of normal days – all sampling periods except July 2015 (Fig. 4.5):

Results of mixing estimation using Flash Diagram for the normal days are shown in Fig. 4.5. The red-dashed line represents the mixing fraction results (after the original groundwater from the limestone layer (L_O) was flashed into the original groundwater from the slaty

greenstone layer (S_0)), whereas the lowest end of red-dashed line indicates Ca^{2+} concentration of S_0 and its top end indicates Ca^{2+} concentration of L_0 . Based on Ca^{2+} concentrations, the mixing fractions of 41% L_0 :59% S_0 and 64% L_0 :36% S_0 from the Flash Diagram corresponded to the representative Ca^{2+} concentration of L-7 and L-11, respectively, while the mixing fractions of 43% L_0 :57% S_0 and 25% L_0 :75% S_0 corresponded to the representative Ca^{2+} concentration of S-3 and S-4, respectively (Fig. 4.5).

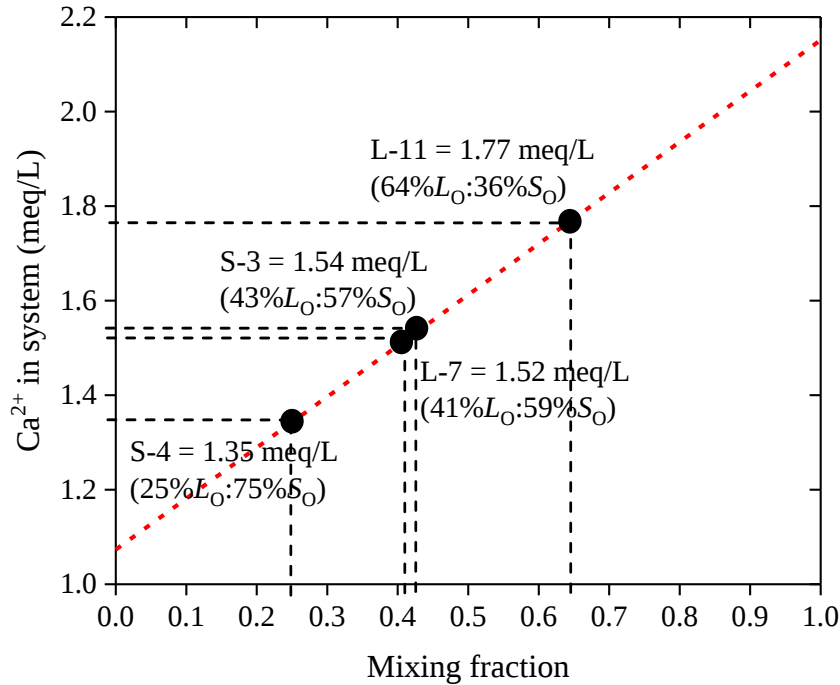


Figure 4.5 Results of mixing estimation using Flash Diagram for the normal days

(2) Case of rainy days – sampling period on July 2015 (Fig. 4.6):

Results of mixing estimation using Flash Diagram for the rainy days are illustrated in Fig. 4.6. Based on Ca^{2+} concentrations, the mixing fractions of 61% L_0 :39% S_0 and 93% L_0 :7% S_0 from the Flash Diagram corresponded to the Ca^{2+} concentration of L-7 and L-11 on the rainy days, respectively, whereas the mixing fractions of 35% L_0 :65% S_0 and 21% L_0 :79% S_0 corresponded to the Ca^{2+} concentration of S-3 and S-4, respectively (Fig. 4.6). These indicate that the mixing fractions of groundwater in the limestone layer in L-7 and L-11 were greater than those of S-3 and S-4 during rainy days, while the mixing fractions of S-3 and S-4 almost remained stable.

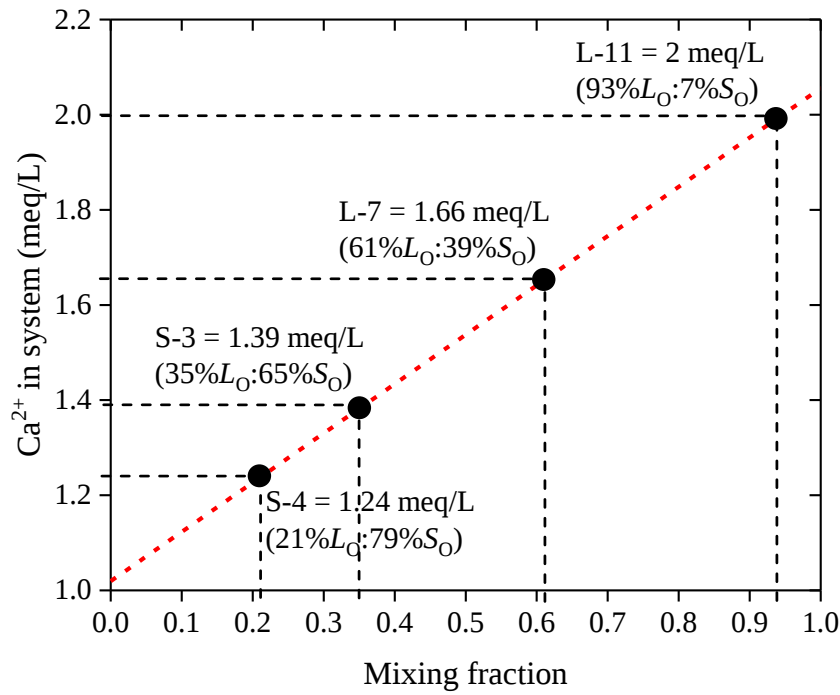


Figure 4.6 Results of mixing estimation using Flash Diagram for the rainy days

From all results of mixing estimation using Ca^{2+} and HCO_3^- concentrations and Flash Diagram function in GWB, the mixing fractions were equal or very close to each other. This suggests that both methods of mixing estimations with the above conditions were reliable and valid to be used for similar issues.

4.3.2 Tritium analysis

Tritium concentrations of the four groundwater samples from the limestone quarry, shallow groundwater from the spring near the quarry and snow sample ranged from less than 0.79 to 2.6 TU (or from less than 0.95×10^{-1} to 3.1×10^{-1} Bq/L) as shown in Table 4.1. From this table, the tritium concentrations were slightly higher in groundwater samples from the limestone layer and the spring, and lower in that from the slaty greenstone layer, while that of snow was the highest. The tritium concentration of groundwater L-7 was lower than those of L-2 and LP-10 but higher than that of S-2, which explains the mixing phenomenon along the interbedded layer, although there were no complete sets of samples.

Table 4.1 Tritium concentration of groundwater samples

Sample name	Sampling date	Measurement results in Bq/L and TU	
		Bq/L ($\times 10^{-1}$)	TU
L-2	2016/08/16	1.7 ± 0.4	1.4 ± 0.3
L-7	2016/08/15	1.3 ± 0.4	1.1 ± 0.3
LP-10	2016/08/16	1.4 ± 0.4	1.2 ± 0.3
S-2	2016/08/16	< 0.95	< 0.79
SW-1	2016/08/16	1.4 ± 0.3	1.2 ± 0.3
Snow	2017/03/01	3.1 ± 0.3	2.6 ± 0.3

※1 TU = 0.118 Bq/L

If the initial tritium concentration of recharged groundwater or the decayed tritium concentration is unknown, the estimation of groundwater age using tritium only provides semi-quantitative, “ballpark” values (Clark and Fritz, 1997). In this quarry, snow and rainwater, however, are mostly the main sources of water forming the groundwater. In case that the initial tritium concentration of recharged groundwater is equal to that of snow, the groundwater age can be determined in the following equation (Bradbury, 1991; Clark and Fritz, 1997):

$$t = \frac{12.43}{\ln 2} \ln \left(\frac{{}^3\text{H}_0}{{}^3\text{H}_t} \right) \quad \text{Equation 4.1}$$

where ${}^3\text{H}_0$ (initial tritium concentration) and ${}^3\text{H}_t$ (tritium concentration at present) are tritium concentrations expressed in TU.

Also, by considering the topographical and hydrological condition, the groundwater is probably young and Equation 4.1 is suitably applicable. After the calculations, we consequently revealed that all groundwater was modern water and the age of groundwater was from 11~14 years in the limestone layer, 15.3 years in the interbedded layer and 17~22 years in the slaty greenstone layer.

In addition, estimation of groundwater age would be more precise if tritium-helium-3 method was applied. As tritium is the radioactive isotope and decays to helium-3 (${}^3\text{He}$) by beta particle emission, thus the measured value of ${}^3\text{He}$ corresponds to atmospheric ${}^3\text{He}$. This represents ${}^3\text{He}$ produced from ${}^3\text{H}$ decay, and is then used in the dating equation (Clark and Fritz, 1997; Motzer, 2007):

$$t = \frac{12.43}{\ln 2} \ln \left(\frac{{}^3\text{He}_t}{{}^3\text{H}_t} + 1 \right) \quad \text{Equation 4.2}$$

where ${}^3\text{H}_t$ (tritium concentration at present) and ${}^3\text{He}_t$ (${}^3\text{He}$ concentration produced from ${}^3\text{H}$ decay) are tritium concentrations expressed in TU.

4.3.3 Overall evaluation for rock slopes

The mixing fractions of groundwater samples L-7 and L-11 significantly varied between normal and rainy days and the groundwater flowing through the limestone layer became dominant on the rainy day, whereas the mixing fractions of groundwater samples S-3 and S-4 were almost stable. The trial results of tritium were also conformed to the mixing phenomenon along the interbedded layer. According to Whitaker and Smart (1997) and Fitts (2002), groundwater integrated in the multi-breaking zones of the interbedded layer erodes limestone by dissolution and widens those breaking zones notably on the rainy day, while calcite is likely to dissolve more in the undersaturated condition. These phenomena induce gradual crack growths and higher groundwater levels during the intense rainfall. Based on Appelo and Postma (2005), the dominant flow mode of groundwater in this study is a conduit flow as suggested by the measured flow rates. It happens along larger fissures and smaller openings formed from dissolution of carbonate rock. Apparently, changes in groundwater level and flow along the interbedded layer may promote pore-water pressure, tension cracks and potential sliding surface, which ultimately lead to a sliding failure along the interbedded layer. Due to the large differences in hydraulic conductivities between the two layers ($4.1 \times 10^{-6} / 4.2 \times 10^{-8} \approx 100$, equal to the considerable ratio reported by Dong *et al.*, 2012), groundwater mixed with rainwater may easily infiltrate and percolate through more permeable

limestone covering layer but not through the slaty greenstone layer. In other words, the slaty greenstone layer with a lower permeability could act as a kind of groundwater barrier and lift the limestone covering layer up. The resultant higher hydraulic head in the limestone covering layer could increase groundwater flow and induce higher dissolution of limestone. The higher groundwater flow and more rapid dissolution of limestone grains will affect the bonds between particles and often reduce the rock strength by more than 25% (Záruba and Mencl, 1976). Regarding the various interpretations, the mixed groundwaters especially L-7 and L-11 along the interbedded layer were identified as sensitive zones affecting the stability of rock slope (Fig. 4.7).

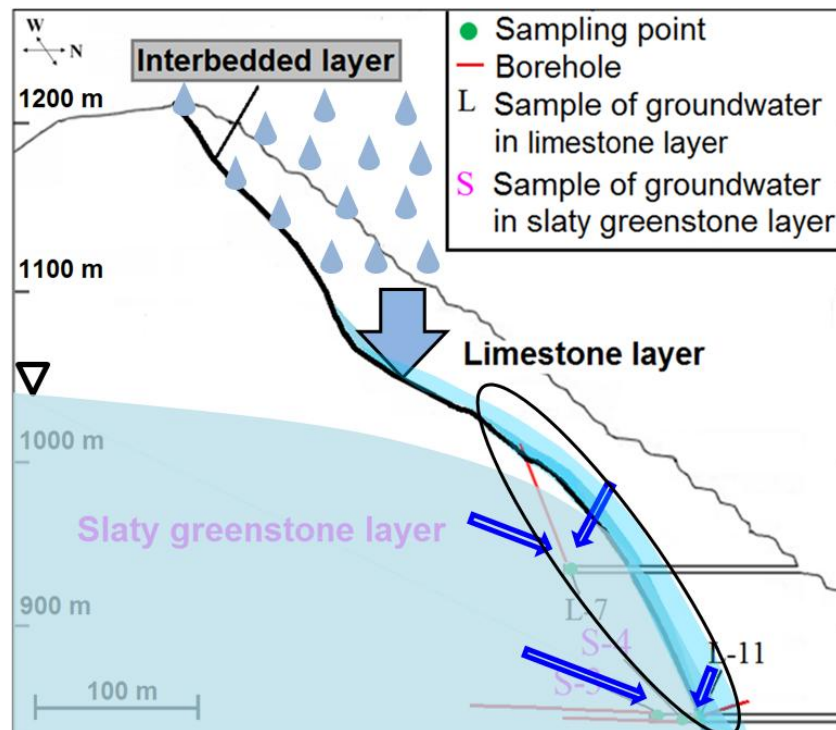


Figure 4.7 Sensitive zones affecting the rock slopes (⇒: blue arrows indicate L-7, L-11, S-3 and S-4 formed by groundwater mixing between the layers; 0: circled area indicates the sensitive zones)

4.4 Conclusions

By using geochemical modeling from GWB and using tritium analysis, the findings of this chapter are summarized as follows:

- (1) The mixing fractions of two groundwater samples (*i.e.*, L-7 and L-11) significantly varied between normal and rainy days, especially the groundwater flowing through the limestone layer became dominant on rainy days.
- (2) The groundwater along the interbedded layer may induce rock slope failure due to a higher mixed fraction on rainy day, which turned the mixed groundwater to be undersaturated with calcite, enhanced dissolution and widened multi-breaking zones in the interbedded layer.

- (3) All groundwater is assumed as modern water through the preliminary results of tritium analysis. The age of groundwater was from 11~14 years in the limestone layer, 15 years in the interbedded layer and older than 17 years in the slaty greenstone layer.
- (4) The results of geochemical modeling and tritium measurement of groundwater were significantly contributed to predict sensitive zones affecting the rock slope and could help to improve the stability of the rock slope by achieving the efficient groundwater abstraction in the sensitive zones.

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CHAPTER 5

GENERAL CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORKS

5.1 General conclusions

Based on the interpretations of all results from various analyses that have been done, the objectives for this whole research have been achieved and satisfied as expectation. Groundwater is a really crucial factor in limestone quarries with regard to rock slope issues. In terms of monitoring and assessment of geochemical properties, evolution and mixing estimation of groundwater of the open-pit limestone quarry, the sensitive zones affecting the stability of rock slopes have been clarified. Tritium analysis was also used for estimation of groundwater age and to support the findings, and the summaries of each chapter in the dissertation are provided accordingly. In Chapter 1, the general introduction of limestone, groundwater managements, groundwater geochemistry and groundwater effects on rock slopes have been addressed. The statement of the problem, objectives of the study and outline of the dissertation were stated to understand the main points of context and the structure of this whole research.

Groundwater flow and its geochemical evolution in mines are important not only in the study of contaminant migration but also in the effective planning of excavation. The effects of groundwater on the stability of rock slopes and other mine constructions especially in limestone quarries are crucial because calcite, the major mineral component of limestone, is moderately soluble in water. In Chapter 2, evolution of groundwater in the limestone quarry located in Chichibu city of Saitama prefecture, Japan was monitored to understand the geochemical processes occurring within the rock strata of the quarry and changes in the chemistry of groundwater, which suggests zones of deformations that may affect the stability of rock slopes. There are three distinct geological formations in the quarry: limestone layer (covering), interbedded layer of limestone and slaty greenstone, and slaty greenstone layer (basement). Although the hydrochemical facies of all groundwater samples were Ca-HCO₃ type water, changes in the geochemical properties of groundwater from the three geological formations were observed. In particular, significant changes in the chemical properties of several groundwater samples along the interbedded layer were observed, which may be attributed to the mixing of groundwater from the limestone and slaty greenstone layers. On the rainy day, the concentrations of Ca²⁺ and HCO₃⁻ in the groundwater fluctuated notably, and the groundwater flowing along the interbedded layer was likely dominated by groundwater from the limestone layer. These suggest that groundwater along the interbedded layer may affect the stability of rock slopes.

Water-rock interaction and groundwater mixing phenomena are important in understanding hydrogeological systems and the stability of rock slopes especially those consisting largely of moderately water-soluble minerals like calcite. In Chapter 3, water-rock interaction in the open-pit limestone quarry was evaluated using PHREEQC, while hierarchical cluster analysis (HCA) and principal component analysis (PCA) were used to classify and identify water sources responsible for possible groundwater mixing within rock layers. The results showed that the water-rock interaction within the quarry was distinguished by individual layers, all of which geochemically evolved as a function of calcite dissolution. The changes in Ca²⁺ and HCO₃⁻ concentrations of several groundwater samples along the interbedded layer found to result from mixing groundwater from the limestone layer and that from slaty greenstone layer. Based on the HCA and PCA results, groundwater samples were

classified into several types depending on their origin: (1) groundwater from the limestone layer (L_O), (2) mixed groundwater flowing along the interbedded layer (*e.g.*, groundwater samples L-7, L-11, S-3 and S-4), and (3) groundwater originating from the slaty greenstone layer (S_O). These results suggest the necessity of continuous monitoring of groundwater.

Estimation of groundwater mixing ratios and tritium analysis are the crucial tasks in groundwater management especially for identifying sensitive zones affecting the rock slopes, while tritium, a radioactive isotope, is effective in predicting groundwater age. In Chapter 4, Geochemist's Workbench was applied to estimate the mixing fractions to clarify sensitive zones that could affect rock slope stability. The mixing fractions of 41% L_O :59% S_O , 64% L_O :36% S_O , 43% L_O :57% S_O and 25% L_O :75% S_O on the normal days corresponded to groundwaters L-7, L-11, S-3 and S-4, respectively, while the mixing fractions of groundwaters L-7 and L-11 (61% L_O :39% S_O and 93% L_O :7% S_O , respectively) on rainy days indicated that the groundwater originating from the limestone layer became dominant. The tritium concentration of groundwater sample L-7 was lower than those of L-2 and LP-10 but higher than that of S-2, which explained the mixing phenomenon along the interbedded layer. All groundwater was found as modern water and the age of groundwater was from 11~14 years in the limestone layer, 15.3 years in the interbedded layer and 17~22 years in the slaty greenstone layer. Regarding overall evaluation for rock slopes, the groundwaters along the interbedded layer significantly affected the stability of rock slopes by enlarging multi-breaking zones in the layer through calcite dissolution and inducing high water pressure, tension cracks and potential sliding plane along this layer particularly during intense rainfall episodes.

5.2 Suggestions for future works

Throughout the findings, the geochemical survey of groundwaters should have been paid attention to every study of rock slope issues, such as rock forming by water-soluble minerals and various geological conditions.

At this stage, this research provided a good result and informative knowledge to the issue. However, this research work is not yet completed and still needs more constructive ideas for the future works. For example, from the trial analysis of tritium, the further tritium analysis is required and more samples should be selected to represent for each layer, *e.g.*, limestone covering layer: L-1, L-3, L-5 and L-10; along interbedded layer: L-7, L-11, S-3 and S-4; and slaty greenstone basement layer: S-1 and S-2. Also, groundwater samples should be conducted on the heavy rain periods to observe their variation and the effects of rainwater. More tritium analysis is also required to clearly confirm the retention time in the quarry, while the ^3H - ^3He analysis method is necessary to obtain more precise groundwater ages.

Furthermore, by means of groundwater geochemistry, precipitation chemistry and mass balance for calcite including estimation of limestone dissolution rate (*e.g.*, kg/year) in the multi-breaking zones or fractures along the interbedded layer would further appear to be significant for rock slopes stability. Measurements of fracture developments are required in the future works and this can be applied by installing measurement sensors in the fractures to record the development of fracture zones along the interbedded layer where rock engineers can assist or take responsibility for this task. If these proposed future works can be done, it may strongly convince researchers of related studies to consider more in these applicable and novel approaches.

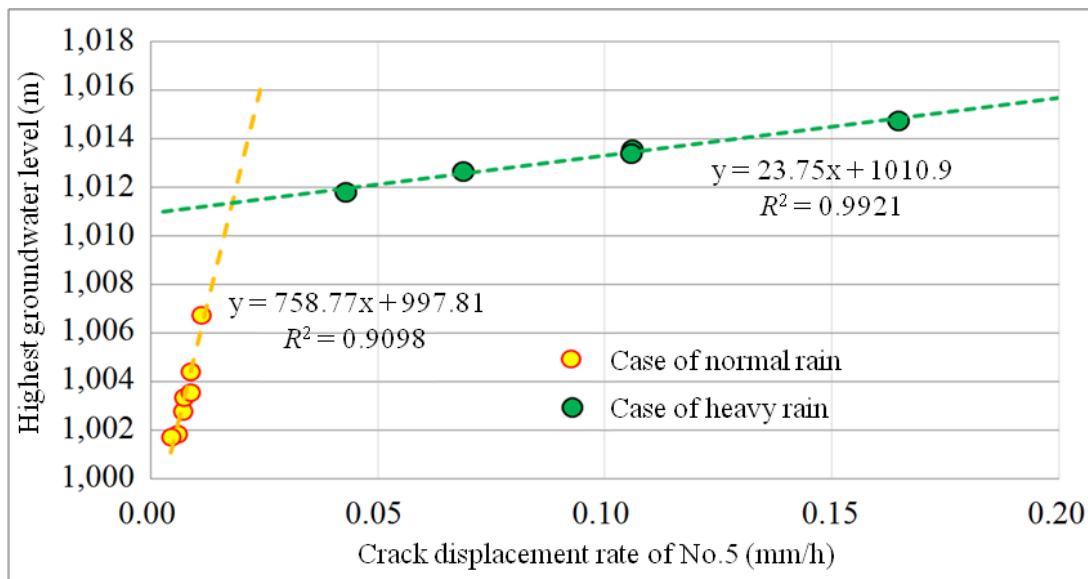
APPENDICES

Appendix A: Supplementary figures

The supplementary figures 1 and 2 mentioned in section 2.3.2 in Chapter 2 of the dissertation were provided as follows:

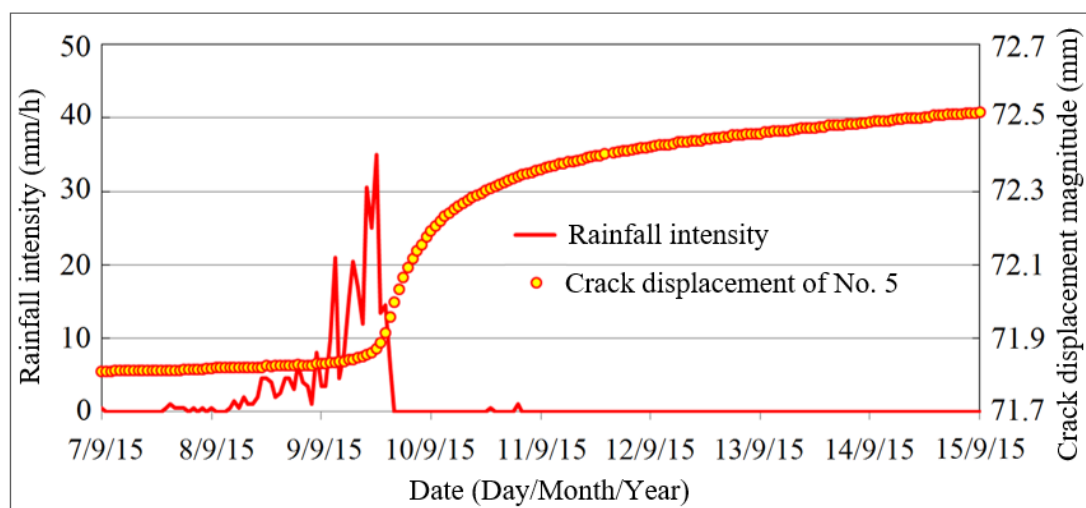
2.3.2 Preliminary results of rock deformation at the site

The positive correlation of crack displacement rate with highest groundwater level in borehole M2010-2 at an elevation of 1,050 m during normal and heavy rains was reported by Ozawa *et al.* (2016) as shown in Supplementary Fig. 1 (Note: The positions of crack displacement meter No.5 and borehole M2010-2 were indicated in Figs. 2.3 and 2.4 of Chapter 2).



Supplementary Fig. 1 Correlation of crack displacement rate (measured by crack displacement meter No.5) with highest groundwater level in borehole M2010-2 at elevation of 1,050 m in case of normal and heavy rains (Ozawa *et al.*, 2016)

Crack displacement behaviors at the time of rainfall from September 07-15, 2015 were conducted by Kondo *et al.* (2016) as illustrated in Supplementary Fig. 2.



Supplementary Fig. 2 Crack displacement (measured by crack displacement meter No.5) behaviors at the time of rainfall from September 07-15, 2015 (Kondo *et al.*, 2016)

Appendix B: Supplementary tables

Supplementary Table 1 Correlation matrix of temperature (T, °C), pH, EC (mS/m), concentrations (mg/L) of dissolved ions and Si of groundwater samples from December 2014 to November 2016

Parameters	T	EC	pH	Na ⁺	Mg ²⁺	K ⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	HCO ₃ ⁻	Si
T	1											
EC	0.447	1										
pH	-0.346	-0.944	1									
Na ⁺	0.075	-0.256	0.182	1								
Mg ²⁺	-0.200	-0.589	0.511	0.863	1							
K ⁺	0.080	-0.020	-0.058	0.546	0.467	1						
Ca ²⁺	0.409	0.971	-0.902	-0.460	-0.758	-0.156	1					
Cl ⁻	0.203	-0.242	0.370	0.043	0.027	-0.158	-0.205	1				
SO ₄ ²⁻	0.547	0.771	-0.702	0.179	-0.223	0.011	0.667	-0.054	1			
NO ₃ ⁻	-0.278	-0.762	0.754	0.457	0.640	-0.118	-0.789	0.320	-0.400	1		
HCO ₃ ⁻	0.324	0.966	-0.926	-0.391	-0.635	-0.015	0.964	-0.345	0.596	-0.830	1	
Si	-0.285	-0.780	0.718	0.757	0.936	0.338	-0.896	0.171	-0.412	0.804	-0.820	1

Supplementary Table 2 Temperature (T, °C), pH, EC (mS/m), ORP (mV), concentrations (mg/L) of dissolved ions and Si of rainwater (RW) collected on July 17, 2015 and snow on March 01, 2017

Sample	T	EC	pH	ORP	Na ⁺	Mg ²⁺	K ⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	HCO ₃ ⁻	Si
RW	23.9	2.37	6.84	143	0.24	< 0.01	0.06	0.68	0.59	0.763	< 0.01	10.98	0.04
Snow	18.2	11	8.6	104	0.34	< 0.01	0.13	7.79	0.67	1.18	1.71	23.18	0.05

Appendix C: List of publications

➤ Conference papers:

Eang Khy Eam, Fujinaga Ryota, Kondo Megumi, Igarashi Toshifumi, 2015. Characterization and evaluation of groundwater from an open-pit limestone quarry in Japan (Oral Presentation). International Symposium on Earth Science and Technology, December 3-4, 2015: Special Issue of the Joint Program of Sustainable Resources Engineering (JPSRE), Kyushu University, 15-03, 11-16.

Eang Khy Eam, Igarashi Toshifumi, Kondo Megumi, Fujinaga Ryota, 2016. Groundwater characteristics of an open-pit limestone quarry and its effects on rock slopes (Oral Presentation). 5th International Doctoral Symposium on Sustainable Management of Resources and Environment in the 21th Century, November 9-11, 2016: Session-Environmental and Resources Geology / Rock Mechanics, Hokkaido University, 19.

Eang Khy Eam, Igarashi Toshifumi, Kondo Megumi, Fujinaga Ryota, 2016. Groundwater characteristics of an open-pit limestone quarry and its effects on rock slopes (Oral Presentation). International Conferences on Earth Sciences and Sustainable Geo-Resources Development, November 14, 2016: Session-Advances in Mining and Tunneling (ICAMT 2016), Hanoi University of Mining and Geology, 133-140.

Eang Khy Eam, Igarashi Toshifumi, Kondo Megumi, Tabelin Carlito Baltazar, Fujinaga Ryota, 2017. Geochemical evolution and groundwater mixing in an open-pit limestone quarry (Oral Presentation). 16th Global Joint Seminar on Geo-Environmental Engineering, May 18-20, 2017: Session-V Abandoned Mines Management, Seoul National University, 319-324.

➤ International journal papers:

Eang Khy Eam, Igarashi Toshifumi, Fujinaga Ryota, Kondo Megumi, Tabelin Carlito Baltazar, 2017. Groundwater monitoring of an open-pit limestone quarry: Groundwater characteristics, evolution and their connections to rock slopes. Environmental Monitoring and Assessment (under review).

Eang Khy Eam, Igarashi Toshifumi, Kondo Megumi, Nakatani Tsurugi, Tabelin Carlito Baltazar, Fujinaga Ryota, 2017. Groundwater monitoring of an open-pit limestone quarry: Water-rock interaction and mixing estimation within the rock layers by geochemical and statistical analyses. International Journal of Mining Science and Technology (under review).

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Looking backward to my childhood, I would have never expected to have such these days. I, the eighth child, grew up in a large family of twelve members comprising of my parents, five brothers, four sisters and me. My family was a business family rather than a farmer family; however, we were living in the average or below average standard but were not too poor. With our huge members, my parents did encourage us to be business persons rather than learners since our long-term expenses on studies without any income were very tough for them to support. Therefore, almost all my siblings became business people except one of my elder brothers and me who could be struggling for a PhD. Perhaps, it was not only our effort but also our predestination, while my other brothers had put their efforts to study but still finally became businessmen. In fact, my actual dream when I was young was to be a medical doctor, but it did not turn out since I have been working well with calculated subjects which led me to incline my interest in engineering. Well, after I worked hard for 5 years for my bachelor's degree in geo-resources and geotechnical engineering at Institute of Technology of Cambodia, 2 years for my master's degree in mineral resources engineering at University of Science Malaysia, I luckily won a doctoral scholarship program to Hokkaido University. Doctoral course was even twice harder than master course. Nevertheless, I still could come to ending after 3 years of the best memories forever with sweet and bitter things coming together. However, this tough achievement was not from me alone, and of course, I would not have made it without all people helped me so far. I, therefore, would like to express my sincere gratitude to all of them as follows:

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