BASIC STUDY ON HYDROGEOCHEMICAL ASSESSMENT OF GROUNDWATER QUALITY IN THE RED RIVER DELTA OF VIETNAM

By

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DEDICATIONS

To my darling life companion, Quang Huy,

To my angel kids, Hannhi & one coming

To my Loving Family

And to all my friends in TMU who have made my life as a doctor student a lot more worthwhile

You've guided me through, encouraged my efforts, endured and shared my failures, applauded my successes, and patiently waited for the culmination of this work, I am forever grateful.

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PREFACE

This dissertation is accomplished as partial fulfillment of my requirements in the doctor course in engineering at the Hydrology and Water Resources Laboratory of the Department of Civil and Environmental Engineering, Graduate school of Urban Environmental Sciences, Tokyo Metropolitan University from Oct. 2011 to Sept. 2014 under the supervision of Professor Akira Kawamura.

The materials in this dissertation are focused mainly on the basic study of hydrogeochemical assessment of groundwater quality, with emphasis on spatio-seasonal hydrogeochemical characteristics of groundwater which are indispensable references for further groundwater analyses required to ensure sustainable groundwater development in the Red River Delta, Vietnam. This dissertation is based mainly on 6 scientific articles that have undergone reviews and assessment in suitable internationally refereed journals. In addition, some parts of this research work have been presented in a number of domestic journals and international conferences.

This study was carried out as a part of the research project, “Solutions for the water-related problems in Asian metropolitan areas” supported by the Tokyo Metropolitan Government, Japan within the program “Asian Human Resources Fund”. Field data were mainly provided by two projects, “National Hydrogeological Database”, and “National Groundwater Monitoring Database” financed by the Department of Geology and Minerals of Vietnam.

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ABSTRACT

In almost all modern civilizations, groundwater is considered as a vital water resource of drinking and domestic use. In the Red River Delta (RRD), the second largest delta in Vietnam including the capital of Hanoi, nearly the entire population depends on groundwater for daily water consumption. Recently, due to the rapid population growth in the RRD, alongside industrial and agricultural developments, the groundwater resources in the region have been overexploited, leading to the unmitigated decline of groundwater levels and deterioration of groundwater quality, which threatens its future availability and suitability for succeeding generations. Sustainable management of groundwater in the RRD is thus necessary to secure its availability and ecological value.

Chemical characteristics of groundwater are important factors determining its quality and utilization. The chemical composition of groundwater is controlled by many factors, including the mineralogy of aquifers, the chemical composition of the rainfall and surface water, climate, topography, and anthropogenic activities. The interaction of groundwater with these factors leads to the formation of different hydrogeochemical characteristics. Therefore, identification of hydrogeochemical characteristics can further the understanding of the geochemical processes, hydrodynamics and origin of groundwater, as well as its interaction with the aquifer materials. However, little information has been available regarding the groundwater hydrogeochemical properties in Vietnam, including the RRD. A study that investigates the hydrogeochemical characteristics of the groundwater on the basis of major ion chemistry is thus necessary to provide fundamental references for further groundwater analyses ensuring sustainable groundwater development in the RRD.

This study focuses on the following main objectives: 1) to investigate the hydrogeochemical characteristics of groundwater in the two main aquifers of the delta, i.e., Pleistocene confined aquifer (PCA) and Holocene unconfined aquifer (HUA), especially the spatio-seasonal changes in the hydrogeochemical properties; 2) to determine the factors controlling the composition of groundwater in the two main aquifers during the dry and rainy seasons. To achieve these goals, the Piper diagram was used to investigate the hydrogeochemical facies, and then the Gibbs diagram was used as reference to determine the factors that govern groundwater composition. Finally, clustering spatio-seasonal hydrogeochemical data to assess the groundwater quality in the delta was carried out using self-organizing maps (SOM) in combination with a hierarchical cluster analysis.

This dissertation is composed of five chapters.

Chapter 1 is the introduction that contains the background, motivation, and objectives of this study. A comprehensive review of literature and a description of the scope and methods were presented in this chapter.

In Chapter 2, the study area and data used were described, taking into account the general geographic and hydro-climatic characteristics of the RRD. This chapter also provided brief descriptions about establishment of the National Groundwater Monitoring Network and National Groundwater Monitoring Database in Vietnam. Groundwater chemistry data, composed of eight major dissolved ions (i.e., Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-}, SO_4^{2-}, and CO_3^{2-}) and total dissolved solids, were collected from 99 groundwater observation wells (52 PCA and 47 HUA wells) during the dry and rainy seasons in 2011 for detecting the spatio-seasonal changes in hydrogeochemical properties.

In Chapter 3, the spatio-seasonal changes in the hydrogeochemical characteristics of groundwater in PCA and HUA of the RRD were investigated by analyzing the physicochemical data using the Piper diagram and Gibbs diagram. Results of the data analysis show that the groundwater in both aquifers in the upstream area of the delta is dominated by the [Ca^{2+}-HCO_3^{-}] water type, while the [Na^{+}-Cl^{-}] dominates along the middle-stream and downstream areas. Seasonal changes in the hydrogeochemical facies in both aquifers were detected in approximately one-third of the sampling wells, which were mainly located at the upstream portion of the delta. The hydrogeochemical facies of PCA were different from that of HUA by about 45% of the sampling wells in both the dry and rainy seasons. These differences were observed mostly in the upstream and middle-stream areas. The Gibbs diagram suggests that the rock-water interaction is the major natural mechanism controlling the chemistry of groundwater in the southwestern part of downstream area of PCA, southwestern part if middle-stream area of HUA, and upstream area of PCA and HUA. Salty paleowater and saltwater intrusion are the main factors that affect the chemistry of groundwater within the rest of the delta.

Chapter 4 further explored spatio-seasonal characteristics of hydrogeochemical data by systematically applying SOM combined with a hierarchical cluster analysis, which serves the purpose of isolating a group of representative clusters that reflect the processes generating the natural variability found in hydrogeochemical parameters. The SOM application classified the hydrogeochemical groundwater data of the PCA and HUA wells into 8 and 5 clusters, respectively, which basically reveal 3 representative water types: high salinity, low salinity, and freshwater. The spatial distribution of these water types were identified in both aquifers. In PCA, the high-salinity type was located in the middle-stream and coastal areas of the delta, while the low-salinity type was observed near the western and northeastern boundaries of the

RRD. In HUA, the high-salinity type was located in the coastal area, whereas the low-salinity type was found not only in the downstream area but also in the northeastern parts of the upstream and middle-stream areas, where groundwater samples were mainly classified into one specific cluster. With closer inspection of land use, the groundwater of this cluster was considered to be contaminated by agricultural activities. Cluster changes from the dry to rainy season were detected in approximately one-third of the PCA wells and one-fifth of the HUA wells. Gibbs diagram was also aptly used to elucidate the cause and significance of the hydrogeochemical characteristics clustered by the SOM. The results suggest that anthropogenic activities (e.g., intensive and long-term irrigation, agricultural fertilization), saltwater intrusion and salt paleowater can be the main factors affecting the chemistry of the groundwater characterized by the low- and high- salinity types.

Chapter 5 presents the overall conclusions and recommendations for groundwater management in the RRD, including the future research works.

PUBLICATIONS

This dissertation is mainly formulated based on six scientific articles as the main milestones of the study which were reviewed and assessed by globally refereed journals. In addition, the some parts of this work have been presented in a number of domestic journals and international conferences. The following list presents the publications which are either published, accepted, or under review. (* means that the content of the paper connect directly to this dissertation.)

Journal Publications

1 D. D. Bui, C. M. Vu, H. S. Nguyen, A. Kawamura, D. M. Vu, T. T. Nguyen, 2011. Trends in hyroclimatic series in Thua Thien Hue province, Vietnam : Rainfall and rainy days. Sustainable Urban Regeneration, No. 8, pp. 40-43.

2* T. T. Nguyen, A. Kawamura, N. Nakagawa, H. Amaguchi, R. L. Gilbuena, 2013. Temporal changes in the hydrochemical facies of groundwater quality in two main aquifers in Hanoi, Vietnam. Proceedings of the 6th International Conference on Water Resources and Environment Research, Germany, pp. 379-387.

3* T. T. Nguyen, A. Kawamura, N. Nakagawa, H. Amaguchi, R. L. Gilbuena, 2014. Spatial classification of groundwater chemistry monitoring data in the Red River Delta, Vietnam using self-organizing maps. Journal of Japan Society of Civil Engineers, Ser. B1 (Hydraulic Engineering), No. 70(4), pp. I_241-I_246.

4* T. T. Nguyen, A. Kawamura, T. N. Tong, N. Nakagawa, H. Amaguchi, R. L. Gilbuena, 2014. Hydrogeochemical characteristics of groundwater from the two main aquifers in the Red River Delta, Vietnam. Journal of Asian Earth Sciences 93, 180-192.

5* T. T. Nguyen, A. Kawamura, T. N. Tong, N. Nakagawa, H. Amaguchi, R. L. Gilbuena, 2014. Hydrogeochemical assessment of groundwater quality during dry and rainy seasons for the two main aquifers in Hanoi, Vietnam. Environmental Earth Sciences. Submitted.

6* T. T. Nguyen, A. Kawamura, D. D. Bui, N. Nakagawa, H. Amaguchi, R. L. Gilbuena, 2014. Clustering spatio-seasonal hydrogeochemical data using self-organizing maps for groundwater quality assessment in the Red River Delta, Vietnam. Water Research. Submitted.

7* T. T. Nguyen, A. Kawamura, T. N. Tong, N. Nakagawa, H. Amaguchi, R. L. Gilbuena, D. D. Bui, 2014. Identification of spatio-seasonal hydrogeochemical characteristics of unconfined groundwater in the Red River Delta, Vietnam. Applied Geochemistry. Submitted.

International Conference Publications

1* T. T. Nguyen, A. Kawamura, C. M. Vu, D. D. Bui, H. Amaguchi, N. Nakagawa, 2011. Quantification of surface water and groundwater interactions by coupling Modflow with Mike 11: a case study in Hanoi, Vietnam. Proceedings of the IHP Symposium on Extreme Events: "Meteorological Hydrological and Tsunami Disasters: Social Adaption and Future", Kyoto, Japan, October 2010, pp. 125 – 134.

2* T. T. Nguyen, A. Kawamura, C. M. Vu, D. D. Bui, H. Amaguchi, N. Nakagawa, 2012. Interactions between the surface water and groundwater of the Red River in Hanoi, Vietnam. Proceedings of the World Environmental and Water Resources Congress 2012, Albuquerque, U.S.A, May 2012, pp. 98-109.

3* T. T. Nguyen, A. Kawamura, T. N. Tong, N. Nakagawa, H. Amaguchi, 2013. Decadal change in the hydrogeochemical facies of groundwater during the dry and rainy seasons in Hanoi, Vietnam. Proceedngs of the Third International MAHASRI/HyARC Workshop on Asian Monsoon and Water Cycle, Da Nang, Vietnam, August 2013, pp. 97-107.

4* T. T. Nguyen, A. Kawamura, N. Nakagawa, H. Amaguchi, 2013. Hydrogeochemical characterisitcs of groundwater in Hanoi, Vietnam. Proceedings of International Symposium on Answers to Asian Aquatic Problem, Tokyo, Japan, November 2013, pp. 19-27.

5* T. T. Nguyen, A. Kawamura, N. Nakagawa, H. Amaguchi, 2014. Application of self-organizing maps for seasonal and spatial classification of the unconfined groundwater hydrogeochemical factors in the Red River Delta, Vietnam. Proceedings of the 20th International conference on Computational Method in Water Resources, June 2014, USB.

Domestic Conference Publications

1* T. T. Nguyen, T. N. Tong, D. D. Bui, 2007. Numerical model in estimation of groundwater balance in Red River Delta based on the relationship between surface and groundwater resources. Proceedings of the 10th Scientific Conference on

Hydrology, Water Resources, and Environent, Hanoi, Vietnam, March 2007, pp. 408-419.

2* T. T. Nguyen, A. Kawamura, N. Nakagawa, H. Amaguchi, R. L. Gilbuena, 2012. An overview of groundwater quality in Hanoi, Vietnam. Proceedings of the 39th Kanto Branch Annual Conference of JSCE, March 2012. CD-ROM : II-16.

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5* 築山裕哉，河村　明，中川直子，天口英雄，T.T. Nguyen, 2014. ベトナム・紅河デルタ全域を対象とした帯水層構造の同定. 第 41 回土木学会関東支部研究発表会講演集，March 2014，CD-ROM：II-64.

6* 山地秀幸，河村　明，中川直子，天口英雄，T.T. Nguyen，2014. ベトナム・紅河デルタにおける被圧地下水の水文地球化学的特性. 第 41 回土木学会関東支部研究発表会講演集，March 2014，CD-ROM：II-66.

7* T. T. Nguyen, A. Kawamura, H. Amaguchi, N. Nakagawa, 2014. Spatio-seasonal analysis of unconfined groundwater quality using self-organizing maps in the Red River Delta, Vietnam. Proceedings of the 2014 Annual Conference of Japan Society of Hydrology and Water Resources, Miyazaki, Japan, September 2014. Submitted.

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CHAPTER 1

INTRODUCTION

1.1 Background and motivation

1.1.1 Groundwater quality assessment as a key process in sustainable development of water resources

In recent decades, groundwater has become one of the most important natural resources in many countries of the world. In its natural state, it is generally of excellent quality and an essential natural resource since water is naturally purified when it is slowly percolating through soil. Comparing with surface water, groundwater has a number of essential advantages: higher quality, well protected from surface contaminants, less susceptible to drought, and much more uniformly spread over large regions than surface water. Groundwater well fields can be constructed and installed gradually in response to growing water demand, whereas hydrotechnical facilities for utilization of surface water often require considerable one time investments. These advantages have resulted in wide use of groundwater for water supply. In some countries in the world such as Denmark, Malta, Saudi Arabia, groundwater is the only source of water supply. In other countries, it is the most important part of total water resources. For example, groundwater in Tunisia is 95% of the country total water resources, 83% in Belgium, 75% in the Netherlands, Germany and Morocco (Igor and Lorne, 2004).

Since the earliest recorded history, groundwater has been regarded as a very good source of clean drink water. It is the main source of municipal domestic and drinking water supply in many countries in the world such as Bulgaria, Hungary, Russia, Italy and Vietnam. The use of groundwater as a source for drinking water has expanded much in recent years and today makes up 25 to 30% of the total water extraction of the world (Younger, 2007). Groundwater withdrawals will continue to increase in the future under the growth of the world's human population. According to

Jury and Vaux (2005), global population will increase by three billion or more over the next 50-75 years, and the number of people living in urban areas will be more than double. To meet increased groundwater demands, knowledge about its availability and sustainability are essential for successful management and future development of this limited resource.

Groundwater availability and sustainability are influenced by many factors, of which is water quality. Water quality generally has been overlooked in some places because of primary focus has been on obtaining a sufficient water supply (McMahon et al., 2007). In some cases, however, water quality may be a limiting factor for some intended used such as drinking and domestic water supply. For example, shallow groundwater beneath irrigated cropland may not be suitable for human consumption because of elevated concentrations of salt, nitrate, or pesticides. The natural quality of groundwater in aquifers is continually being modified by the influence of man. This occurs due to groundwater abstraction and the consequent change in groundwater flow, artificial recharge and direct inputs of anthropogenic substances. A clear understanding of the status and trends in water quality conditions and the natural and anthropogenic processes that control them facilitates more robust assessments of groundwater availability and sustainability. In other words, assessment of groundwater quality is a key process in sustainable development of water resources.

Groundwater is the most precious and valuable natural resource in Vietnam in general and in the Red River Delta (RRD) in particular. All its residents depend entirely on groundwater for their domestic water supply because of the uneven distribution and poor quality of surface water resources. In particular, in Hanoi, the capital of Vietnam, almost 100% of drinking water is from groundwater resources (Bui, 2011). Therefore, groundwater is vital for socio-economic growth, quality of life and environmental sustainability. In recent years, due to the rapid population growth in the RRD, alongside industrial and agricultural developments, the groundwater resources in the region were overexploited, leading to the unmitigated decline of groundwater levels (Bui et al., 2012) and deterioration of groundwater quality (Duong et al., 2003; Montaganero et al., 2007), which threatens its future availability and/or suitability for succeeding generations.

1.1.2 Problem statement and literature review.

Groundwater overexploitation, a condition in which the rates of extraction from an aquifer exceed the rates of recharge by water percolating form above, occurs in almost every region of the world. The impacts of overexploitation have been reported widely. It has caused critical changes in patterns of groundwater flow to and from adjacent aquifer systems and serious groundwater level decline in many areas over the world. Groundwater level declines may affect the environment for plants and animals. For example, plants in the riparian zone that grew because of the close proximity of the water table to the land surface may not survive as the depth to water increases. Groundwater level decline is an indicator of groundwater depletion and aquifer degradation, which threatens aquifer sustainable development (Akther et al., 2009). Other obvious impacts are saltwater intrusion and land subsidence, which threaten the integrity of groundwater resources in different locales around the world. Likewise, surface waters including river flows, lake levels and wetland levels are also affected by reduced groundwater discharges (Konikow and Kendy, 2005) and then ecosystems might be affected adversely (Zektser et al., 2005).

Future groundwater supplies are also threatened by declines in water quality caused by pollution. Wherever agriculture becomes modernized, dramatic increase occur in nitrate- and pesticide- loading of nearby surface and ground waters. In certain soils, enhanced drainage from agricultural operations can leach toxic metals from the subsurface to surface and ground waters. In areas where adequate sanitation services are absent, growing populations inevitably lead to increased levels of pathogens in water supplies. Decades of land disposal or accidental release of untreated toxic waste have created a serious groundwater contamination problem in many areas, and much of the waste still lies in the soil. Groundwater contamination is extremely expensive to remediate, and it is unlikely that developing countries will have the resources in the future to support significant remediation efforts (Jury and Vaux, 2005)

In the RRD, the second largest delta in Vietnam, clean water demands arising from the rapid expansion of industry, population, and services has been becoming rather urgent. The amount of groundwater abstraction has been rapidly and continuously increasing. The excessive groundwater withdrawal without the wise management and adequate understanding of hydrogeochemical characteristics have caused some serious problems, such as: drying up of shallow wells, decline of groundwater level, land subsidence, and groundwater pollution in this area (Bui et al., 2011). Prober sustainable management of groundwater in the RRD is thus necessary to secure its availability and ecological value.

Chemical characteristic of groundwater is an important factor determining its quality and utilization. Therefore, understanding the hydrogeochemical characteristics of groundwater is crucial for groundwater planning and management, which should be conducted adequately prior to other studies. Generally, the motion of groundwater along its flow paths below the ground surface increases the concentration of chemical species. Hence, the groundwater chemistry could reveal important information on the geological history of the aquifers and the suitability of groundwater for domestic, industrial and agricultural purposed (Aghazaded and Mogaddam, 2010). Hydrogeochemical evaluation of groundwater system is usually based on the availability of a large amount of information concerning groundwater chemistry (Hossien, 2004). Groundwater chemistry, in turn, depends on a number of factors, such as general geology, degree of chemical weathering of the various rock types, quality of recharge water and inputs from sources rather than water-rock interaction. Such factors and their interactions result in a complex groundwater quality (Sunne et al., 2005).

Around the world, many studies have been carried out to investigate and evaluate the hydrogeochemistry of groundwater. For example, Ahmed et al. (2013) investigated the main factors and mechanisms that control groundwater salinization and hydrogeochemical processes in the Eastern Nile Delta, Egypt. Li et al. (2012) assessed groundwater quality for irrigation purposes and investigated the hydrogeochemical evolution mechanisms in Pengyang County, China. Baghvand et al. (2010) studied the groundwater quality of the Kashan Basin, central Iran, and characterized the groundwater species. Marghade et al. (2012) assessed the chemistry of the major ions of shallow groundwater to understand the groundwater geochemical evolution and water quality in Nagpur city, central India. Arumugan and Elangovan (2009) assessed the groundwater quality of the Tirupur region in India for drinking and irrigation purposes.

In Vietnam, due to the importance of groundwater in the RRD as well as the region's importance in the development of Vietnam, in recent years several studies on groundwater have been carried out. Tran et al. (2012) investigated the origin and extent of fresh groundwater, salty paleowaters, and saltwater from recent seawater intrusions in the RRD using geological observations, geophysical borehole logging, and transient electromagnetic methods. Arsenic pollution of groundwater in the entire RRD has been studied by Winkel et al. (2011) on the basis of a complete geo-referenced database from several hundred wells. Other groundwater-related studies in the RRD targeted the capital of Hanoi. Duong et al. (2003), for example, considered the groundwater pollution in water supplies of Hanoi. Groundwater arsenic contamination was identified in some parts of Hanoi (Berg et al., 2001). Trinh and Fredlund (2000) investigated the land subsidence due to excessive groundwater exploitation in Hanoi. Until recent years little work has been done to explore the relationships which are known to exist between hydrogeology and chemical characteristics of groundwater in a specific environment. Data on the chemical quality of groundwater has been collected from many locations in the RRD but no adequate interpretation of the hydrogeologic relationships underlying the regional distribution of the chemical constituents is available.

In the past, the study by Schoeller (1959) suggested that the chemical composition of groundwater in a delta does not, in general, remain constant in time and space. As water moves from its recharge area through the aquifer its concentration tends to increase because groundwater gains mineral constituents as it moves through the delta. Seaber (1965), who studied the variations in chemical character of groundwater from the Englishtown formation underlying the Atlantic Coastal Plain in New Jersey, also shows that the chemical character of groundwater of the same aquifer progressively changes as the water moves away from its recharge area. Differences in chemical quality of groundwater, therefore, are related to the mineralogy and texture of the sediments and in general, reflect the regional variation in geologic character of the aquifer. In other words, the differences in chemical quality from place to place are the result of several interdependent factors. Probably the more important factors are the physical and chemical properties of the material through which the water moves, source and amount of recharge, geology of the derivative rocks in the drainage basin before recharge and the direction of groundwater movement. Regional patterns of chemical quality in groundwater exist but in some cases the quality of water from wells is influenced more by local conditions (Smoor, 1967).

In most studies of groundwater quality, little quantitative information is available to define any of the possible relationships between groundwater quality and the hydrogeology. The main difficulty, perhaps, lies in the fact that although numerous chemical analyses of groundwater are available, rarely these chemical analyses are from wells located and drilled with the specific purpose of conducting a study of groundwater quality. In the case of the RRD, chemical analyses of wells were made to comply with public health regulations or as a standard procedure rather than with the objective to study the regional distribution of groundwater quality. In addition, the problem is one of how to deduce or test assumed relationships from an essentially incomplete set of chemical analyses not adequately representing all the hydrologic and geologic factors involved.

In order to identify the spatio-seasonal hydrogeochemical characteristics of groundwater, it is essential for a robust classification scheme to cluster water chemistry samples into homogeneous groups (Güler and Thyne, 2004). Several common clustering techniques have been utilized in order to divide groundwater samples into similar homogeneous groups (each representing a hydrogeochemical facies) with the ultimate objective of characterizing the quality of groundwater, such as principal component analyses (Monjerezi et al., 2011), Q- and R- mode hierarchical cluster analysis (Reghunath et al., 2002), and fuzzy c-means clustering technique (Güler and Thyne, 2004). These methods are efficient at grouping water samples by chemical similarities, but are not useful for the visual assessment of the results and presentation of maps showing hydrogeochemical facies (Güler et al., 2002). The recently proposed method of the self-organizing maps (SOM) is likely to become an alternative or complementary tool of those clustering methods (Iseri et al., 2009).

The SOM is a powerful technique capable of ordering multivariate data by similarity, while preserving the topological structure of the data (Kokonen, 2001). Based on an unsupervised learning algorithm, the SOM has excellent visualization capabilities, including techniques that use the reference vectors of the SOM to give an informative picture of the data (Hong et al., 2003). The SOM has been implemented in various aspects of water research, e.g., classification of environmental monitoring data (Jin et al., 2011) and clustering for wastewater treatment monitoring (Hilario et al., 2004). The SOM has also proven to be a powerful and effective data analysis tool in meteorological analysis and detection of long-term changes in climate (Nishiyama et al., 2007; Leloup et al., 2007). The application of self-organizing maps has not tested for hydrogeochemical data to investigate the spatio-seasonal hydrogeochemical characteristics.

1.2 Objectives, scope, and methods

Given the above-mentioned concerns, this dissertation focuses on the following main objectives: 1) to investigate the hydrogeochemical characteristics of groundwater in the RRD, especially the spatio-seasonal changes in the hydrogeochemical properties; 2) to determine the factors controlling the composition of groundwater.

To achieve these goals, the Piper diagram was used to classify the major ions in the groundwater into various hydrogeochemical types in order to investigate and identify the hydrogeochemical facies. Then, the Gibbs diagram was used as reference to determine the factors that govern groundwater composition. An understanding of the dominant controls on the groundwater composition is prerequisite to a more exact formulation and eventually correct representation of groundwater quality system.

Finally, clustering spatial-seasonal hydrogeochemical data to assess the groundwater quality in the delta was carried out using self-organizing maps in combination with a hierarchical cluster analysis.

1.3 Outline of the dissertation

This dissertation is composed of five chapters.

Chapter 1 is the introduction with contains the background, motivation, and objectives of this study. A comprehensive review of literature and a description of the scopes and method were presented in this chapter.

In Chapter 2, the study area and data used in this study were described, taking into account the general geographic and hydro-climatic characteristics of the RRD.

In Chapter 3, the spatial and seasonal changes in the hydrogeochemical characteristics of groundwater in the two main aquifers of the RRD were investigated by analyzing the physicochemical data in the Delta's Holocene unconfined aquifer and Pleistocene confined aquifer using the Piper and Gibbs diagrams.

Chapter 4 further explored spatio-seasonal characteristics of hydrogeochemical data by systematically applying SOM combined with a hierarchical cluster analysis. The SOM was systematically applied using a stepwise procedure, including transformation of data, establishment of the SOM structure, initialization of reference vectors, parameters training, selection of an optimal number of clusters, and a fine-tuning cluster analysis. The first, second, and third quartiles of the reference vectors were plotted on radar charts to display the fundamental characteristics of each cluster. In addition, Gibbs diagram was also created to elucidate the hydrogeochemical characteristics classified by the SOM.

Chapter 5 presents the overall conclusions and recommendations for groundwater management in the RRD, including the future research works.

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CHAPTER 2

STUDY AREA AND DATA USED

2.1 Study area

A delta is an area of low, flat land (sometimes shaped like a triangle) that is formed from the deposition of the sediment carried by a river over a long period of time and created at the mouth of a river (Bui, 2011). In this study, the Red River Delta (RRD) is thus defined as the area whose surface is covered with sediments within the border shown in **Fig. 2-1**.

The RRD located in the northern part of Vietnam is the most developed region of Vienam comprising 11 provinces and cities (Hanoi, Hai Phong, Vinh Phuc, Ha Nam, Bac Ninh, Hai Duong, Hung Yen, Nam Dinh, Thai Binh, Quang Ninh and Hai

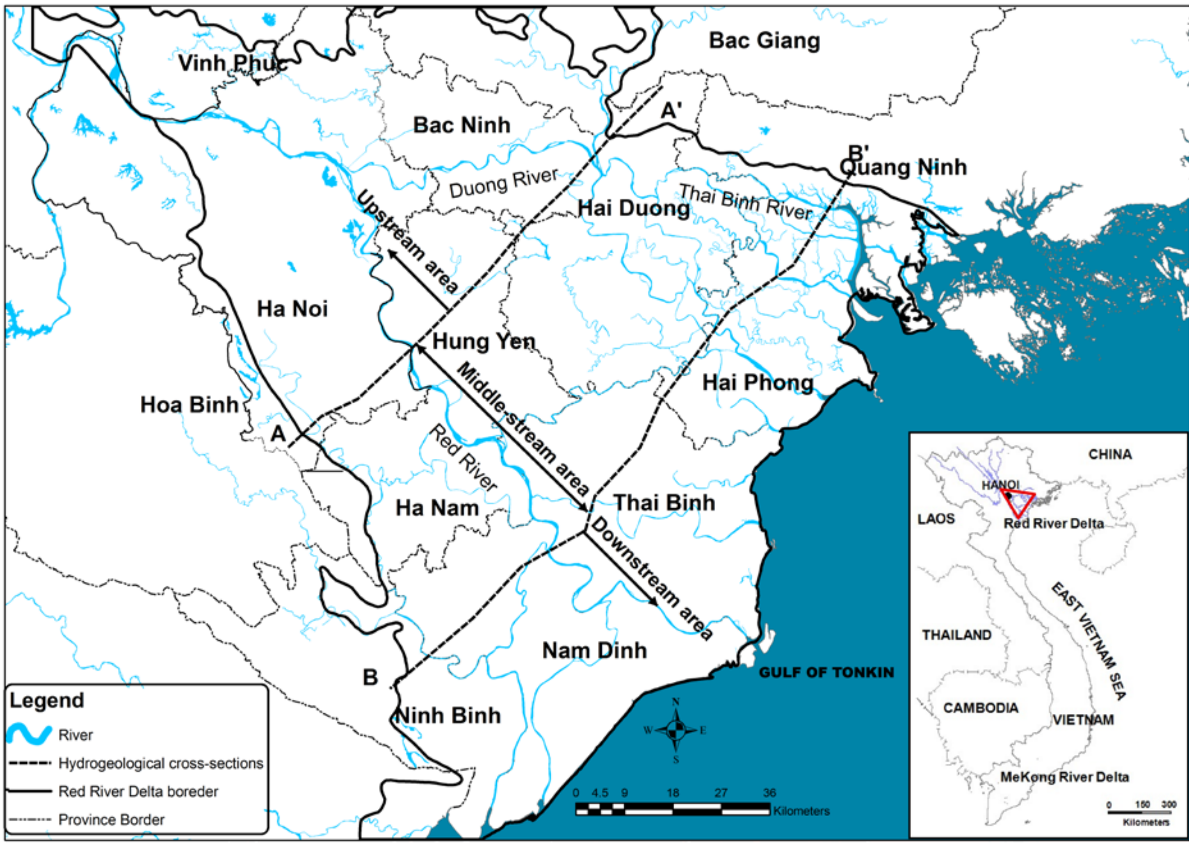

Fig. 2-1 Location of the Red River Delta in Vietnam

Duong) as shown in **Fig. 2-1**. Many important centers of economy in Vietnam such as: Hanoi, Hai Phong, Nam Dinh are located there (Bui et al., 2011).

The RRD, located on the west coast of the Gulf of Tonkin (Bac Bo), is one of the largest deltas in Southeast Asia. It formed by the Red River, which originates in the mountains of Yunnan province in China (Tanabe et al., 2003). The RRD plain measures about 150km from its apex at Viet Tri south-eastwards to the coastline, where the subaqueous delta front extends offshore for 10-20 km. At the coast the delta is about 130km across (Mathes and Zalasiewicz, 1999). The delta area is about 13,000 km^2 and is surrounded by a mountainous region composed of Precambrian crystalline rocks and Paleozoic to Mesozoic sedimentary rocks. The NW-SE-aligned Red River fault system regulates the distribution of the mountainous area, the drainage area and the straight course of the Red River. However, fault movements have been considerably minor since the late Miocene (Nielsen et al., 1999). Very long time ago, the RRD is fertilized by sediment of Red River system when it is flood plain without dike system and free from the sea. Under the natural conditions a dense river system is created and developed. Recently, due to the socio-economic activities and country development, a river dike system was constructed to separate land with rivers and to form low-lying sub areas in different provinces as present with slight difference in elevation. When river dike system was constructed, sediment is directly transported to the sea to form new land. That's why a sea dike system is also constructed to prevent hinterland from the natural disasters. With the time being, some sea dike lines are moving towards the sea and created artificial sub areas of new land between sea dikes. The major type of topography is flood plain whose elevation is mainly below 12 m above mean sea level (MSL) with about 55% of less than 2 m. (Bui et al., 2011).

The RRD is situated in the tropical monsoonal region with two distinct seasons: the rainy (May to October) and dry (November to April) seasons. The annual average rainfall is about 1,600 mm, 75% of which occurs during the rainy season. In the rainy season, flood is quite severe but very low flows exist in the dry season. The average discharge of the Red River at the Hanoi station is 1160 m^3/s during the dry season and

3970 m^3/s during the rainy season (IMHE-MONRE, 2011). The annual average humidity is about 80%, and the average temperature is 24^{o}C. The annual evaporation average is around 900 mm (Bui et al., 2011).

The river network is quite extensive, with a network density of about 0.7 km/km^2. The total length of the main Red River system is about 1,126 km from the source in China to the Gulf of Tonkin in the East Vietnam Sea, of which the main branch of the Red River in the delta accounts for 216 km. The main Red River branch enters the delta at Son Tay, and then divides into two major distributaries in the vicinity of Hanoi: the Red River to the southwest and the Thai Binh River to the northeast. The Thai Binh River carries only 20% of total water discharge (Tanabe et al., 2003). In the Red River, high concentration of suspended solids is always present that actually give it its "reddish" color. The total sediment discharge and water discharge of the Red River System is 100-1300 million t/yr and 120 km^3/yr, respectively (Pruszak et al., 2002), and the average sediment concentration of the river is 0.83-1.08 kg/m^3. Approximately 90% of the annual sediment discharge occurs during the rainy season, at which time the sediment concentration may reach 12 kg/m^3 (Tanabe et al., 2003).

The Red River estuarine system comprises 9 estuary branches: Cua Cam, Lach Tray, Van Uc, Thai Binh, Diem Dien, Tra ly, Ba lat, Ninh Co, and Cua Day. These branches form typical lowland rivers with large floodplains that are regularly inundated under high tidal conditions. The width of the main channel under tidally averaged conditions varies from 200-500m, and the width between main dikes is few kilometers. At estuary mouths, the average channel depth and width are approximately 4 m below the mean water level and approximately 700 m, respectively (Nguyen et al., 2012). The mean tidal range is 2.0-2.6 m, and the maximum tidal range is 3.2-4.0 m along the Red River coast (Mathers and Zalasiewicz, 1999). In the summer monsoon season, tidal influences within the delta are restricted because of the overwhelming effect of the high freshwater discharge, but in the dry season, tidal effects are evident in all of the major distributaries almost as far inland as Hanoi (Mathers et al., 1996). The distance of seawater intrusion in the dry season is larger than that in the flood season, although it is affected by the morphology of the estuary. It should be noted that tidal current easily penetrates through wider and deeper river mouth. Offshore salinity in the Tonkin gulf is stable throughout a year: i.e. 33‰ in the dry season and 32 ‰ in the flood season (observed at the Bach Long Vi Island). Due to the longshore current and the freshwater discharge from the rivers, coastal salinity is slightly lower: The observed value was 25 - 26 ‰ at most river mouths.

The RRD has a population of around 20.2 million people in 2012 (around 23% of Vietnam's total population), making it one of Vietnam's most densely populated regions (Vietnam General Statistic Office, 2013). The population density, 1,160 inhabitants/km^2 is five times the national average. Of the entire population, 70% live in rural area, but the number of people living in urban areas is increasing rapidly, especially in the Hanoi area, leading to a strong increase in consumption of natural resources and energy and in production of waste (Luu et al., 2010).

About 47% of the area is used as agricultural and aquacultural land; of this, 90% (6,700 km^2) is used for annual crops, 6.6% for aquaculture and fisheries, 3.1% for perennial crops, and 0.6% as pasture area. Only 13% (2,000 km^2) is classified as forest area, situated mostly in the western side of the RRD (Hoa Binh province). Hosing, industry, roads, and canals occupy 21% of the delta total area, while about 12% are water surfaces (river, lakes, etc.) (Vietnam General Statistic Office, 2013). The main income in most provinces within the RRD is from agriculture. In recent years, the economic structure in the basin has been changing significantly. Employment has gradually been reduced in the agricultural sector and shifted to industry and service sectors, causing a large migration from rural areas to urban ones (Luu et al., 2012).

The lakes, ponds and canals in highly urbanized areas are seriously polluted with untreated domestic and industrial wastewater. The groundwater, being relatively cleaner and generally unaffected by the surface environmental problems, has become the most trusted freshwater source in the RRD (Bui et al., 2011). The amount of groundwater abstraction has been rapidly increasing. Excessive groundwater exploitation without wise management and adequate understanding of aquifer system and fluctuation of groundwater levels has caused many serious problems, such as: groundwater pollution, groundwater level decline, land subsidence, and seawater intrusion as mentioned in the introduction. The concentrations of some groundwater quality indices like ammonia, arsenic, and other heavy metals have increased over the years (Agusa et al., 2005; Berg et al., 2001; UNICEF Vietnam, 2001). In the RRD, Hanoi is the most urbanized city, and its water supply almost entirely depended on groundwater resources, achieving sustainable development of groundwater resources in Hanoi is much more important than any other cities and provinces.

In terms of regional geology, the RRD is composed of Quaternary-aged unconsolidated sediments with the thickness ranging from a few meters in the northwest to 150-200 m at the coastline in the southeast (Tran et al., 2012). In Bui et al.'s studies (2011), five hydrogeological cross-sections were identified by hydrostratigraphically interpolating strata data from a number of well logs in order to demonstrate the vertical framework of the aquifer system. In order to facilitate investigation of spatial hydrogechemical characteristics, the RRD was divided into three parts: upstream, middle-stream, and downstream by two lines, AA' and BB', as shown in **Fig. 2-1**. The two lines are the lines connecting boreholes of two typical hydrogeological cross-sections. **Fig. 2-2** shows two out of the five cross-sections along the A-A' and B-B' lines shown in **Fig. 2-1**.

The groundwater mostly exists as porous water that forms the topmost Holocene unconfined (HUA) and the shallow Pleistocene confined aquifer (PCA), lying over the Neogene water- bearing layer (NWL) and sandwiching the Holocene-Pleistocene aquitard. This aquitard is mainly composed of slightly permeable or impermeable materials like silty clay, clay sand and clays. It has low permeability, less than 0.1 m/day. However, in some minor places in Hanoi, this aquitard is completely missing, which create hydrogeological windows resulting in total connectivity between the two aquifer systems. Therefore, groundwater levels of the two aquifers are highly interconnected. HUA consists of silty clay and various sands mixed with gravel. The thickness of this layer varies greatly up to more than 60 m, which increases from the northwest to the southeast of the delta, whereas there exists a thin area with the thickness of less than 30 m in the middle of the delta. The transmissivities in HUA vary up to 2200 m^2/day. PCA consists of sands mixed with cobbles and pebbles, and is situated below HUA in the stratigraphic sequence. The thickness of PCA fluctuates over a large range with an average of about 80m, and gradually increases from the northwest to southeast of the delta. The transmissivity ranges from 700 to 3000 m^2/day and indicates a very high potential of groundwater resources. NWL is mainly formed by geological cracks, weather erosion and unconsolidated sediments. The materials of NWL include: cemented gravel, cemented clay, arkosic sanstone, argillite, and clay carbon. The NWL has very limited groundwater potential with existence of cleft and karst water. The Red River is an important natural recharge source for groundwater storage in Hanoi because it runs

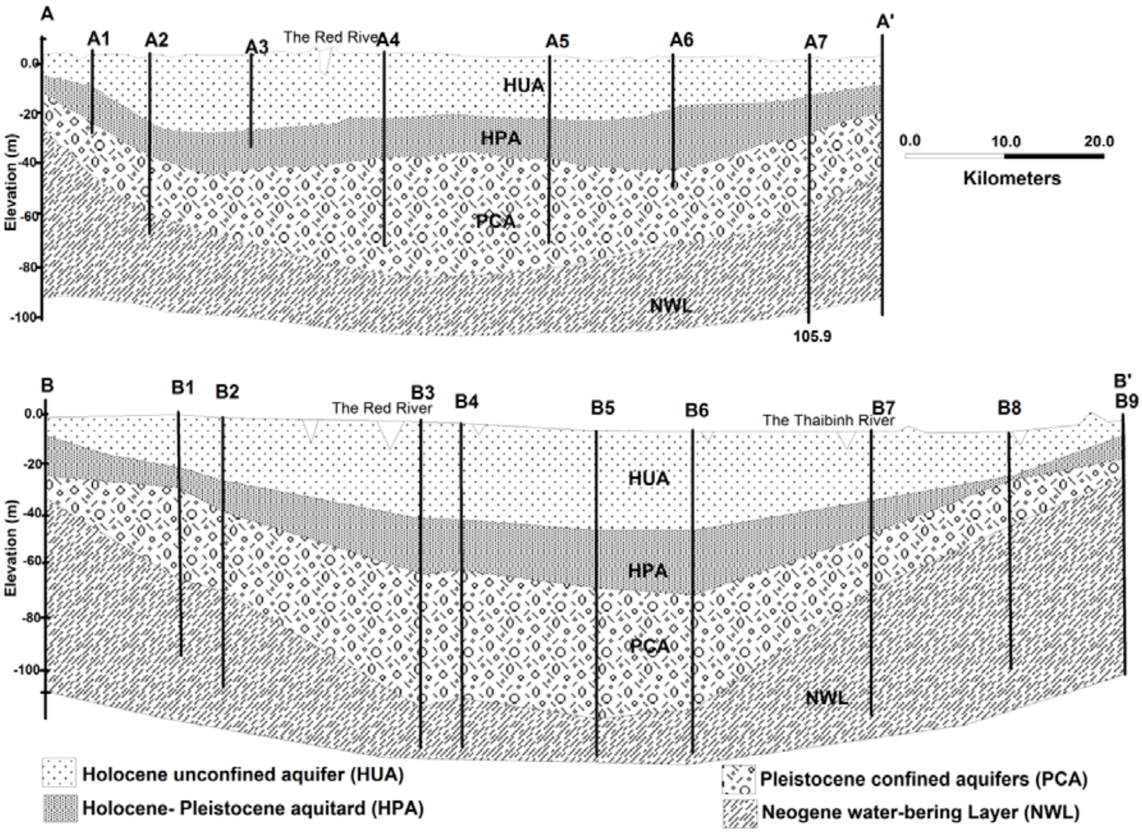

Fig. 2-2 Hydrogeological cross-sections along A-A', B-B' lines as shown in Fig. 2-1 (from Bui et al., 2011)

across HUA and in some places across PCA due to stream-bed erosion. The seasonality in groundwater levels for both HUA and PCA is closely associated with the annual cycles of river-water levels (Bui et al. 2012). Within the 5 km zone of the Red River, HUA and PCA are mainly recharged by the river. Outside the 5 km zone, PCA is predominantly recharged mainly by the surrounding mountain range and the vertical percolation of water coming from HUA through hydrogeological windows.

According to Bui et al. 2011, HUA groundwater levels are usually situated within 4 meters under the ground surface. Their annual cycle was strongly governed by those of rainfall and river water level with average amplitude of about 2m. On the other hand, PCA groundwater levels showed rapid decline trends over the area with a speed of about 0.2 m/year. Groundwater in Hanoi receives mostly recharges from surface water because shallow aquifers adjacent to river mostly experience great groundwater recharge.

2.2 Hydrogeochemical data set

As important as groundwater levels, monitoring data of groundwater chemical variables are also extremely important for groundwater management and assessment. The chemical characteristics of groundwater are an important factor determining its quality and utilization. Groundwater quality monitoring, especially the chemical composition of groundwater can help to determine annual and long- term changes of groundwater quality, understand how aquifer systems interact with climate and surface water, etc. (Hussein, 2004). In Vietnam, however, detailed information and long term data for groundwater assessment were rare, which is an obstacle for the application of integrated groundwater management on a large basin scale. The Vietnamese government had been investing much money in setting up groundwater observation wells since 1989. However, it was not until 1995 when a fairly wide groundwater monitoring network was set up and has gone into operation in the delta. The major objectives of the monitoring program were identified: (1) describe general changes of groundwater quality and quantity for each hydrogeologic unit (2) defined long term trends (if any); and identify the major factors that influence groundwater quality and quantity (Bui, 2011).

The groundwater data recorded by the groundwater monitoring network in Vietnam mentioned previously are huge but not systematically organized, and only accessible to a very limited number of users. These primary data sets came from various sources, and have large differences in data format, quality, and storage media. Therefore, a time-consuming and costly project for better management and utilization of observed data was initiated in 2000 under the support and nomination of the Vietnam Department of Geology and Minerals, in which we constructed and have maintained a GIS-based groundwater monitoring database (GMD). The groundwater monitoring database were established to maintain groundwater data observed by three main groundwater monitoring networks for three main areas of principal groundwater withdrawals in Vietnam: (1) the RRD; (2) the Mekong River Delta; and (3) the Western Highlands or Central Highlands of Vietnam. The basic data for groundwater, such as groundwater level, temperature, and quality are being monitored. Record lengths and intervals highly vary depending on the completion time, the intended uses of the observation wells, and variables to be monitored (Bui, 2011). Basically, the groundwater quality data are measured twice per year during the dry and rainy seasons. Details about this project and the database were described in the final report of the project (Tong, 2004).

To take advantage of the data from the National Hydrogeological Database Project, we used the most recent groundwater chemical data, which were collected from 52 PCA and 47 HUA observation wells in the months of February (dry season) and August (rainy season) in 2011 to investigate the hydrogeochemical characteristics of groundwater in the RRD. The chemical data used in this study are as follows: total dissolve solids (TDS), pH, major cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}), major anions (HCO_3^-, Cl^- and SO_4^{2-}), NH_4^+, NO_2^-, and NO_3^-. The carbonate ion (CO_3^{2-}) concentration was calculated from the observed bicarbonate (HCO_3^-) concentration and pH data (James, 1982).

Figs. 2-3 and **2-4** show the 52 and 47 groundwater sampling wells in the PCA and HUA, respectively, which are numbered from Well Nos. 1–31 for both conjunctive PCA and HUA wells, from 32–52 are for the PCA wells and from 53–68

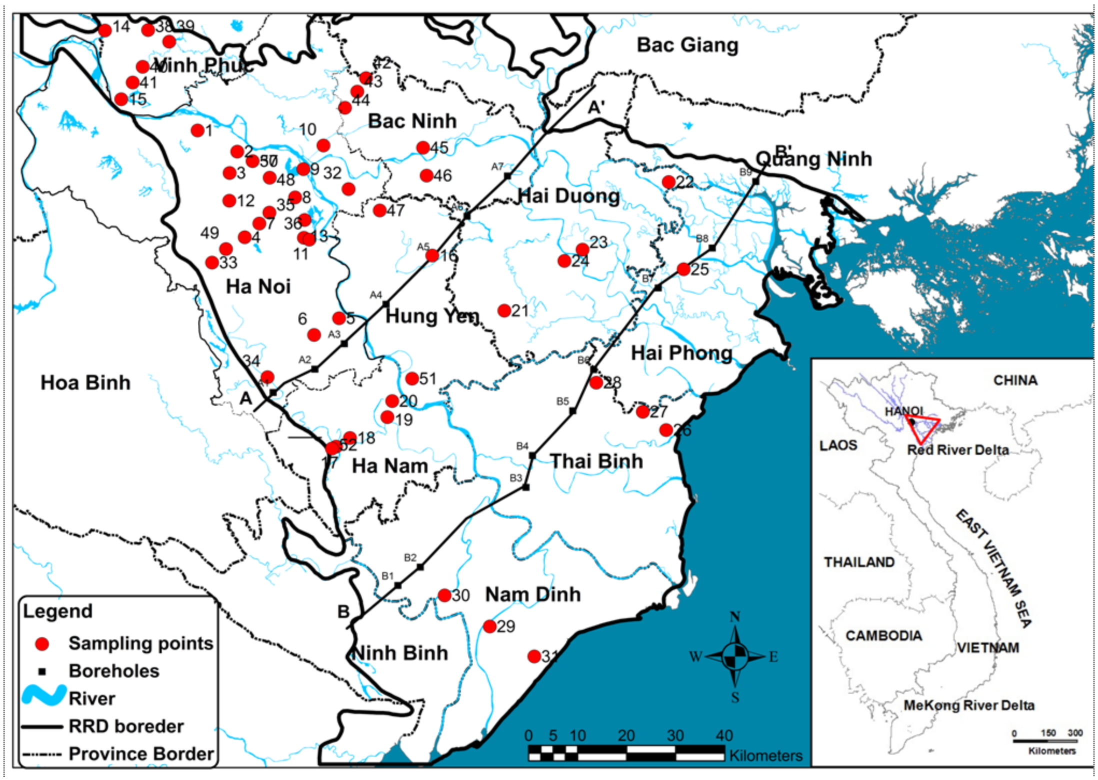

Fig. 2-3 Location of Pleistocene confined groundwater observation wells

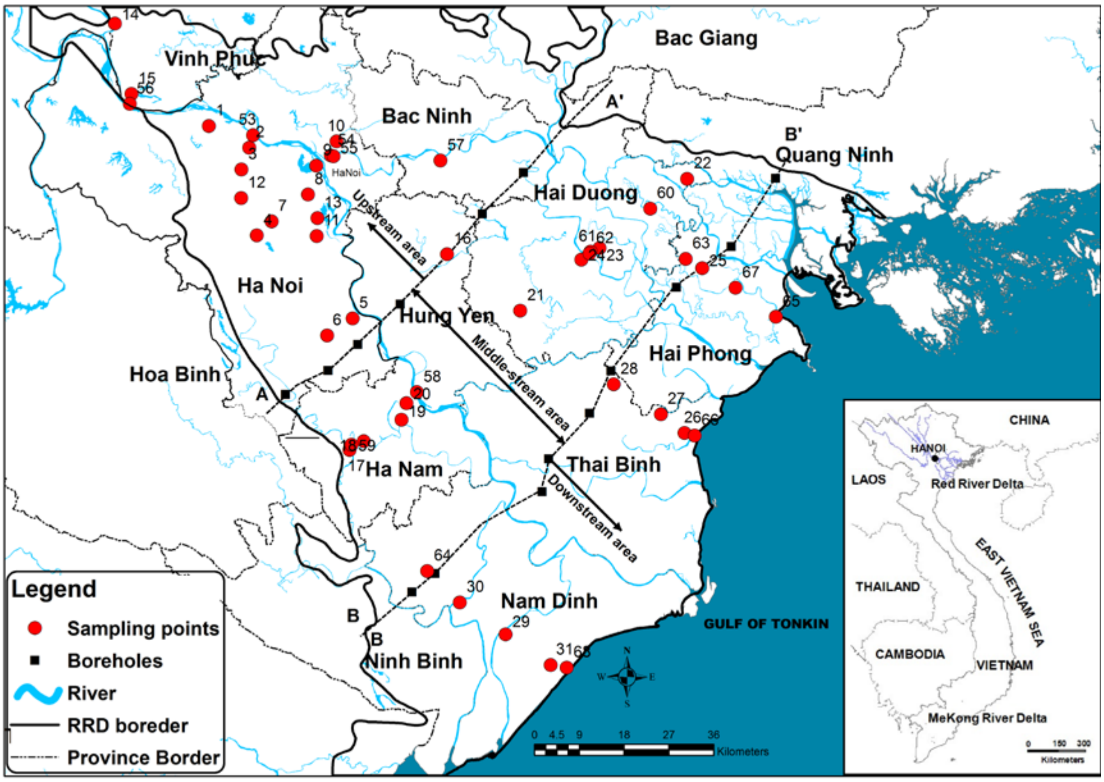

Fig. 2-4 Location of Holocene unconfined groundwater observation wells

for HUA wells . Well Nos. 1–15, 32-50 and 53–57 are in the upstream area; Well Nos. 16–24, 51, 52 and 58–64 are in the middle-stream area; and Well Nos. 25–31 and 65–68 are in the downstream area.

2.3 Methods of chemical analyzes

Groundwater samples were collected throughout Hanoi from observation wells. Sampling was done in accordance to the guidance on the sampling, preservation and handling of groundwater samples of Ministry of Natural Resources and Environment (MONRE, 2008). All samples were filtered with 0.45-µm filter membranes and collected in clean and dry Polyethylene or Polytetrafluoroethylene plastic bottles filled to the top and capped tightly to avoid evaporation and exchanges of sample water with atmospheric materials. To take account of any physicochemical change that might take place, all field-based water parameters such as temperature and pH were measured in situ.

Chemical analyses were undertaken at the laboratory of Analytical Chemistry Department, Vietnam Academy of Science and Technology, following the national technical regulation on underground water quality (MONRE 2008). This regulation was based on ISO standards. Major cation concentrations were analyzed by the EDTA titrimetric method for Ca^{2+} and Mg^{2+} (ISO 6058 1984; ISO 6059 1984) and the flame emission spectrometry method for Na^{+} and K^{+} (ISO 9964-3 1993). Calibrations for cations analyses were carried out by appropriate standards. Both laboratory and international reference materials were used to check the accuracy of the chemical analyzes. The concentrations of Cl^{-}, HCO_3^{-}, and SO_4^{2-} anions were determined using Silver nitrate titration on chromate indicator (Mohr’s method), ion chromatography and continuous flow analysis (CFA) methods, respectively (ISO 9297 1989; ISO 22743 2006). To determine the concentrations of NH_4^{+}, NO_2^{-}, and NO_3^{-}, the dimethulphenol spectrometric method, molecular absorption spectrometric method and spectrometric method using sulfosalicylic acid were applied, respectively (ISO 7150-2 1986; ISO 6777 1984; ISO 7890-3 1988). The analytical precision for measurement of ions was determined by calculating the ionic balance error, which was within 5%.

2.4 Conclusions

Groundwater has been the primary source of daily water supplies for people living in the RRD, the second largest delta in Vietnam. Excessive groundwater withdrawal in the absence of wise management and adequate understanding of the hydrogeochemical characteristics has caused serious problems, such as the unmitigated decline of groundwater levels and the deterioration of water quality. Therefore, it is essential to investigate the hydrogeochemical characteristics of groundwater in the RRD of Vietnam to provide fundamental information for sound groundwater management and development.

Hydrogeochemical evaluation of groundwater systems is usually carried out with the availability of a large amount of groundwater chemical data (Hussein, 2004). The reliability and validity of groundwater assessment strongly depend on the availability of a large volume of high-quality data. In Vietnam, observation data on groundwater chemistry were scarce, which has been an obstacle in the implementation of even the most basic studies on groundwater quality. Motivated by these necessities, the Vietnamese Government had been investing funds in the setting up of groundwater quality observation wells. The volume of groundwater chemical data collected through this project is huge, but not yet analyzed nor systematically organized prior to this study. These primary data sets came from various sources and have large differences in data format, quality and storage media. Hence, a time-consuming and costly project named the “National Hydrogeological Database Project” was initiated in 2000 under the support of the Vietnam Department of Geology and Minerals, in which one of the authors was nominated as project leader to construct the GIS-based hydrogeological database.

The RRD has the most extensive hydrogeochemical database in Vietnam with a large number of data owners. However, the record lengths and intervals vary greatly depending on the completion time and the intended usage of the observation wells, as well as the aquifers and variables that are being monitored. In this study, the hydrogeochemical data of 99 observation wells (52 Pleistocene confined wells and 47 Holocene unconfined) during the dry and rainy season in 2011 were used to investigate spatio-seasonal hydrogeochemical characteristics of groundwater. Hopefully, these data sets will be available to the public in the next stage, because without these data sets it is very hard to implement necessary groundwater assessment ensuring sustainable groundwater development in the delta.

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CHAPTER 3

HYDROGEOCHEMICAL ASSESSMENT OF GROUNDWATER QUALITY BY PIPER DIAGRAM AND GIBB DIAGRAM

3.1 Introduction

The Red River Delta (RRD) is the second largest delta in Vietnam with an area of about 13,000 km^2 which encompasses the Vietnamese capital, Hanoi. The RRD has a population of around 20.2 million people in 2012 (around 23% of Vietnam's total population), making it one of Vietnam's most densely populated regions (Vietnam General Statistic Office, 2013). In terms of groundwater uses, almost all of the residents of the RRD depend entirely on groundwater for their domestic water supply. In recent years, due to the rapid population growth in the RRD, alongside industrial and agricultural developments, the groundwater resources in the region were overexploited, leading to the unmitigated decline of groundwater levels (Bui et al., 2012) and deterioration of groundwater quality (Duong et al., 2003; Montaganero et al., 2007), which threatens its future availability and/or suitability for succeeding generations. Sustainable management of groundwater in the RRD is thus necessary to secure its availability and ecological value.

In the past, a few RRD's groundwater–related studies were carried out, covering only a small part of the delta, specifically in Hanoi (Vietnam's capital). For instance, Trinh and Fredlund (2000) investigated the occurrence of land subsidence in the Hanoi area as caused by excessive groundwater exploitation. Duong et al. (2003) investigated the prevalence of water pollution in the groundwater supplies of Hanoi. However, in recent years several studies on groundwater have been accomplished in the whole RRD due to the region's importance in the development of Vietnam. For example, Tran et al. (2012) investigated the origin and extent of fresh groundwater, salty paleowaters and saltwater from recent seawater intrusions in the RRD by using geological observations, geophysical borehole logging and transient electromagnetic methods. Arsenic pollution of groundwater in the entire RRD has been studied by

Winkel et al. (2011) based on a complete geo-referenced database with 37 chemical parameters from several hundred wells. In our earlier studies, the authors investigated the spatial characteristics of the aquifer system (Bui et al., 2011) as well as groundwater level trends in the whole RRD (Bui et al., 2012). So far, there has been no study carried out in the RRD that focused on analysis of the hydrogeochemical parameters (major cations and anions) such as hydrogeochemical facies, which is fundamental and could serve as reference to future groundwater research works in Vietnam.

The chemical composition of groundwater is controlled by many factors, including the mineralogy of aquifers, the chemical composition of the precipitation and surface water, climate, topography, and anthropogenic activities (Edmunds et al., 1982). The interaction of groundwater with these factors leads to the formation of different hydrogeochemical facies (Clark and Fritz, 1997). Hydrogeochemical facies is one of the most effective tools used to differentiate various forms of geochemical reaction and can be used to infer environmental factors that affect groundwater quality and its flow. Identification and analysis of the hydrogeochemical facies can help further understand the geochemical processes, hydrodynamics and origin of groundwater, as well as its interaction with the aquifer materials (Furi et al., 2011).

The chemistry of groundwater has been extensively studied by many researchers in the past. For instance, Marghade et al. (2012) assessed the chemistry of major ions of shallow groundwater to understand the groundwater geochemical evolution and water quality in Nagpur city in India. Baghvand et al. (2010) studied the groundwater quality of the Kashan Basin in Iran, and characterized the groundwater species using the Piper diagram. Al-Shaibani (2008) evaluated the groundwater chemistry of a shallow alluvial aquifer in western Saudi Arabia. Most of the earlier studies focused only on the hydrogeochemical properties of shallow (unconfined) aquifers. In Vietnam, there is no study on the hydrogeochemical facies of either unconfined or confined aquifers as far as the authors know. Groundwater in the RRD mainly exists in the Holocene unconfined aquifer (HUA) and Pleistocene confined aquifer (PCA) with the latter serving as the highest groundwater potential and most important aquifer for water supply (Bui et al., 2011). In addition, excessive groundwater abstraction from PCA causes vertical percolation of water from HUA, which may lead to changes in groundwater chemistry. Therefore, the investigation of the differences in hydrogeochemical characteristics between HUA and PCA is important in understanding the interaction between the two aquifers.

Groundwater interacts with surface hydrologic systems, such as rivers, lakes and oceans, and is indirectly influenced by seasonal changes during recharge and discharge. The change in seasons can potentially affect the hydrogeochemical properties of groundwater, especially in areas that have distinct dry and rainy seasons, like Vietnam. The hydrogeochemical characteristics in the RRD can also be affected by the change in seasons, hence, investigation of the seasonal changes in the hydrochemistry of groundwater may reflect the groundwater hydrodynamics and circulation that may help improve the data collection programs for groundwater assessment and enable better use of groundwater supplies in the RRD.

The aim of this study is to investigate the seasonal changes and spatial hydrogeochemical characteristics of groundwater in not only HUA but also PCA in the RRD. Through the initiative of the national government (National Hydrogeological Database Project), groundwater quality data of the HUA and PCA in the RRD were collected in 2011 during the dry and rainy seasons. The Piper diagram was used to investigate and identify the hydrogeochemical facies. Decades of studies (e.g. Back, 1966; Raji and Alagbe, 1997; Kagabu et al., 2011) have already proven the efficacy and robustness of the Piper diagram method in classifying the ions in the groundwater into various hydrogeochemical types. Gibbs (1970) proposed chemical diagrams for the assessment of functional sources of dissolved chemical constituents and to infer the mechanism controlling the chemistry of surface water. Various researchers have already demonstrated the usefulness of Gibbs diagram for groundwater of shallow (unconfined) aquifers (Xiao et al., 2012; Oinam et al., 2012; Raju et al., 2011). In this study, the Gibbs diagram was used as reference to determine the factors that govern groundwater composition, not only in the unconfined aquifer, but also in the confined aquifer of the RRD. This study will provide valuable insights in understanding the changes from the dry to rainy seasons, the differences between two aquifers, and the spatial distribution of the groundwater hydrogeochemical properties in the RRD.

3.2 Methods

3.2.1 Piper diagram

The term "hydrogeochemical facies" is used to describe the occurrence modes of groundwater in an aquifer with respect to chemical composition. To determine the hydrogeochemical facies of groundwater, the percentages of the equivalents of each species of major ion are plotted on a Piper diagram. This diagram is then used to identify the dominant cation and anion in each well by using the left and right ternary diagrams, respectively. The left ternary diagram is divided into three cationic classification regions, namely the [Ca^{2+}], [Mg^{2+}], and [Na^{+}] types. The right ternary diagram is divided into three anionic classification regions, the [HCO_3^{-}], [Cl^{-}], and [SO_4^{2-}] types (Piper, 1944). Each observation has a dominant cation and anion type. The combination of these predominating ion types is the hydrogeochemical facies of the aquifer at a specific observation well. After plotting the data, the hydrogeochemical facies of each well in both aquifers were investigated for spatial distributions and seasonal changes by comparing their dominant ions.

3.2.2 Gibbs diagram

To determine the major natural mechanisms controlling the composition of dissolved solids, chemical diagrams which were proposed by Gibbs (1970) can be used. The weight ratios Na/(Na+Ca) and Cl/(Cl+HCO_3) were plotted against TDS separately on a logarithmic axis to represent the Gibbs cation and Gibbs anion diagrams, respectively. The Gibbs diagram was originally used to evaluate surface waters, but recent groundwater quality studies used these diagrams to assess the sources of dissolved chemical constituents of groundwater in shallow (unconfined) aquifers, which have high potential for being influenced by surface water (Marghade et al., 2012, Xiao et al., 2012; Raju et al., 2011). According to Gibbs (1970), the three major natural mechanisms controlling surface water chemistry are precipitation dominance, rock dominance, and evaporation dominance. Evaporation of surface water and moisture in the unsaturated zone has been found as the most influential process in the development of the chemical composition of shallow groundwater (Richter and Keitler 1993). Evaporation concentrates the remaining water and leads to precipitation and deposition of evaporates that are eventually leached into the deeper aquifer (Zhu et al. 2008). In addition, as mentioned above, in the RRD there are two main aquifers: HUA and PCA with the latter serving as the most important aquifer for the water supply, and groundwater levels of two aquifers (HUA and PCA) are highly interconnected in some parts of the study area. Therefore, Gibbs diagram will be a useful tool to analyze geochemical processes of groundwater in both unconfined and confined aquifers in the study area. This study is the first attempt to use the Gibbs diagram as reference for assessing the factors governing groundwater chemistry in a confined aquifer as well as an unconfined aquifer of the RRD.

3.3 Result and discussion

3.3.1 Chemical quality of groundwater

The statistical ranges and means of the monitored hydrogeochemical parameters in HUA and PCA, and their comparison with the Vietnamese drinking water standards are listed in **Tables 3-1** and **3-2**, respectively. Using these tables the suitability of groundwater in the RRD for drinking and domestic use was evaluated. By comparing **Tables 3-1** and **3-2**, the concentrations of most ions in HUA are generally higher than those in PCA in both the dry and rainy seasons. This is due to the evaporation of water in the unsaturated zone, which increases the concentration of inorganic salts that would leach into the HUA groundwater (Ahmed, 2013). The obvious influence of rainfall on the river water chemistry was pointed out by Al-Shaibani (2008) such as the reduction of sodium, potassium, and chloride concentrations, as well as TDS. As shown in **Tables 3-1** and **3-2**, the concentrations of most ions decrease from the dry to the rainy season in both aquifers, indicating that the groundwater samples were affected as well during the rainy season. This also implies a fast recharge of groundwater from the river. Furthermore, in the RRD, the seasonality in groundwater level for both HUA and PCA is closely associated with the annual cycles of rainfall and river water levels (Bui et al., 2012). Hence, rainfall and river recharge may create a dilution effect, which could explain the downward trends in the ion concentration during the rainy season in both aquifers in the RRD. It was also observed that more samples for both aquifers exceeded the Vietnamese drinking water standards (in terms of TDS, Na^+, Cl^-, SO_4^{2-}, NH_4^+, NO_2^-) in the dry season than in the rainy season.

These tables also show that most groundwater samples from both aquifers in the middle-stream (from Well Nos. 16 to 24) and downstream areas of the delta (from Well Nos. 25 to 31) have exceeded the Vietnamese drinking water standards for TDS, Na^+ and Cl^-, which provided good evidence regarding the impact of salty paleowater or salt water intrusion on groundwater chemistry in the middle-stream and downstream areas (Tran et al., 2012).

High nitrite and nitrate concentrations in water can cause serious deleterious effects to humans, particularly the disease called methemoglobinemia or the 'blue baby' syndrome. Sources of these nitrogen compounds often come from fertilizers, manure, refuse dumps and industrial wastes. In the RRD, more than 80% and all samples in both aquifers have concentrations of nitrite and nitrate within the permissible level of the Vietnamese drinking water standard, as shown in **Tables 3-1** and **3-2**, which indicate a relatively good water quality for most of the groundwater sources. However, high ammonium concentrations were detected in more than 65% of the total samples in both aquifers. Ammonium does not pose any serious health threat, but in natural waters it tends to convert into either nitrite or nitrate. Ammonium, thus, can be considered as potential source for nitrite and nitrate ions. High concentration of nitrogen compounds may also indicate groundwater contamination resulting from urbanization, industrial and agricultural activities (Keith, 2002). Therefore, monitoring nitrogen concentrations may help in effective management of groundwater resources in the RRD.

Table 3-1 Range of chemical parameters in HUA and their comparison with the Vietnamese standards for drinking water

Chemical parameter	Vietnamese standard value (maximum limit)	Concentrations of ions in the dry season			Concentrations of ions in the rainy season		
		Range	Mean	Sample numbers exceeding desirable limits	Range	Mean	Sample numbers exceeding desirable limits
pH	6.5-8.5	6.5-8.1	7.2	none	6.5-8.1	7.5	none
TDS (mg/L)	1000	116-7212	1642	3,16,21,22, 23, 24, 26, 27, 29, 30	133-6576	1269.2	3, 16, 22, 23, 26, 27, 29, 30, 31
Ca^{2+} (mg/L)	-	21.04-190.38	86.3		20.04-160.32	82.8	
Mg^{2+}(mg/L)	-	4.59-252.32	69.8		7.6-224.96	61.2	
Na^{+} (mg/L)	200	3.5-2240	408.8	3, 21, 23, 24, 26, 27, 29, 30, 31	3.8-2050	294.1	3, 21, 22, 23, 26, 27, 29, 30, 31
K^{+} (mg/L)	-	0.8-87	18.9		0.6-89	14.94	
HCO_3^{-} (mg/L)	-	57.97-1217.35	471.8		82.38-1238.71	455.93	
SO_4^{2-}(mg/L)	250	0-946.19	59.1	3,16	0-685.58	42.96	3,16
Cl^{-} (mg/L)	250	6.2-4200.83	724.9	3,21, 22, 23, 24,26, 27, 28, 29, 30, 31	6.2-3855.19	518.6	3, 21, 22, 23, 26, 27, 29, 30, 31
CO_3^{2-} (mg/L)	-	0.000-0.003	0.0004	none	0.000-0.0041	0.0006	none
NH_4^{+} (mg/L)	1.5	0-80	10.22	2, 3, 4,5, 6, 7, 8, 13, 18, 20, 21, 22, 23, 24, 26, 29, 30, 31	0-53.6	10.1	1, 2, 3, 4, 6, 7, 8, 13, 15, 18, 19, 20, 21, 22, 23, 25, 26, 27, 28, 29, 30, 31
NO_2^{-} (mg/L)	3	0-50	9.12	3, 19, 20, 23, 26, 27, 28, 29, 30, 31	0-0.92	1.78	3,26, 27, 28
NO_3^{-} (mg/L)	50	0-6	0.99	none	0-3.6	0.19	none

Table 3-2 Range of chemical parameters in PCA and their comparison with the Vietnamese standards for drinking water

Chemical parameter	Vietnamese standard value (maximum limit)	Concentrations of ions in the dry season			Concentrations of ions in the rainy season		
		Range	Mean	Sample numbers exceeding desirable limits	Range	Mean	Sample numbers exceeding desirable limits
pH	6.5-8.5	6.17-8.35	7.2	24	6.24-8.38	7.4	22,27
TDS (mg/L)	1000	145-10071	1231.9	6, 16, 18, 20, 22, 23, 24, 25, 26, 28, 31	161-3180	832.5	6,18,20,23,24,26
Ca^{2+} (mg/L)	-	18.04-205.4	73.7		15.03-197.9	65.8	
Mg^{2+}(mg/L)	-	5.87-249.3	50.23		9.73-110.96	37.08	
Na^{+} (mg/L)	200	4-3300	304.4	6, 18, 20, 23, 24, 26, 28, 29, 31	5.25-942.5	156.2	6,20,23,24,26,29
K^{+} (mg/L)	-	1.25-197.5	16.97		0.95-42	6.76	
HCO_3^- (mg/L)	-	15.26-814.62	274.2		15.4-619.35	253.6	
SO_4^{2-}(mg/L)	250	0-456.3	30.4	16	0-195.35	16.53	none
Cl^- (mg/L)	250	7.09-6292.38	626.32	6, 17, 18, 20-31	1.08-1949.7	343.63	6, 17, 18,20-27, 29, 30
CO_3^{2-} (mg/L)	-	0.000-0.0024	0.0003	none	0.000-0.0017	0.00024	none
NH_4^+ (mg/L)	1.5	0-80	12.43	1,2,3, 4,6, 7, 8, 10, 11, 12, 13, 14,17, 18, 19, 20, 23, 24, 26, 28, 29, 30	0-70.4	9.12	1, 2, 3, 4,6, 7, 8,11, 12, 13, 14,17, 18, 19, 20, 22, 23, 24, 26,27,29
NO_2^- (mg/L)	3	0-24	2.92	19,23,31	0-3.8	0.36	2
NO_3^- (mg/L)	50	0-15.2	0.88	none	0-3.01	0.216	none

These tables also show that most groundwater samples from both aquifers in the middle-stream (from Well Nos. 16 to 24) and downstream areas of the delta (from Well Nos. 25 to 31) have exceeded the Vietnamese drinking water standards for TDS, Na^+ and Cl^-, which provided good evidence regarding the impact of salty paleowater or salt water intrusion on groundwater chemistry in the middle-stream and downstream areas (Tran et al., 2012).

High nitrite and nitrate concentrations in water can cause serious deleterious effects to humans, particularly the disease called methemoglobinemia or the 'blue baby' syndrome. Sources of these nitrogen compounds often come from fertilizers, manure, refuse dumps and industrial wastes. In the RRD, more than 80% and all samples in both aquifers have concentrations of nitrite and nitrate within the permissible level of the Vietnamese drinking water standard, as shown in **Tables 3-1** and **3-2**, which indicate a relatively good water quality for most of the groundwater sources. However, high ammonium concentrations were detected in more than 65% of the total samples in both aquifers. Ammonium does not pose any serious health threat, but in natural waters it tends to convert into either nitrite or nitrate. Ammonium, thus, can be considered as potential source for nitrite and nitrate ions. High concentration of nitrogen compounds may also indicate groundwater contamination resulting from urbanization, industrial and agricultural activities (Keith, 2002). Therefore, monitoring nitrogen concentrations may help in effective management of groundwater resources in the RRD.

3.3.2 Hydrogeochemical facies of groundwater

Fig. 3-1 shows the Piper diagram plot for PCA. The numerical symbols in the figure correspond to the locations of the observation wells in **Fig. 2-3**. The non-bold and bold symbols correspond to the dry and rainy seasons, respectively. Based on the left ternary diagram in **Fig. 3-1**, 24 and 33 out of the 62 groundwater samples (for both dry and rainy seasons) were identified as [Ca^{2+}] and [Na^+] types, respectively, while only 5 samples are of [Mg^{2+}] type. Based on the right ternary diagram, 30 and 31out of the 62 groundwater samples were [HCO_3^-] and [Cl^-] types, respectively, while only one sample is of [SO_4^{2-}]

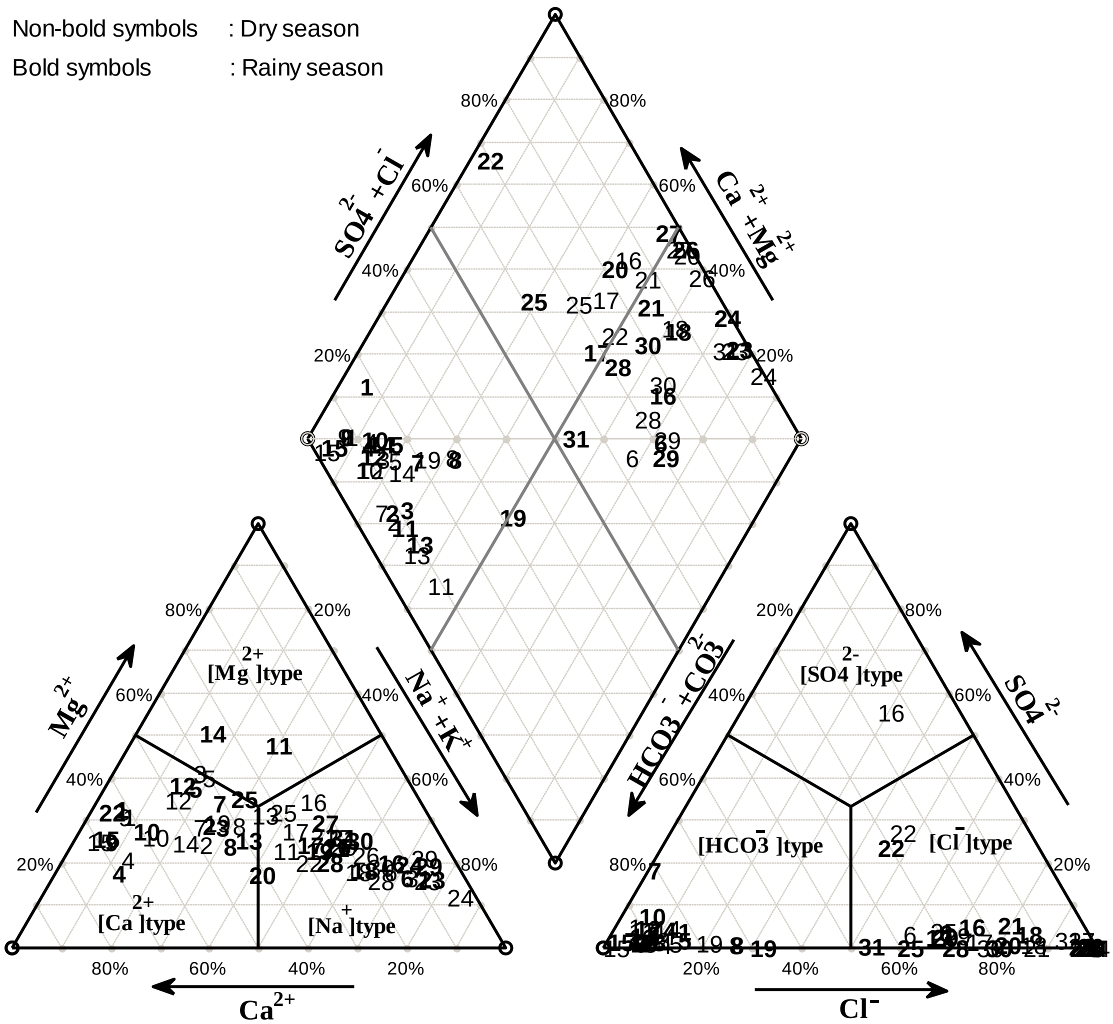

Fig. 3-1 Piper diagram for Pleistocene confined groundwater in the RRD

type. To examine the differences in the hydrogeochemical facies between HUA and PCA, the Piper diagram for HUA was also created as shown in **Fig. 3-2**. From the left ternary diagram, 31 and 26 out of the 62 groundwater samples (for both dry and rainy seasons) are of [Ca^{2+}] and [Na^{+}] types, respectively, while 5 samples are of [Mg^{2+}] type. The right ternary diagram on the other hand shows 41 and 19 samples to be of the [HCO_3^-] and [Cl^-] types, respectively, while two samples are shown to be of the [SO_4^{2-}] type.

To have a better view of the distribution of water type in the RRD, **Figs. 3-3** and **3-4** were created for PCA and HUA, respectively. The black and white symbols represent the cation-anion water types of the groundwater for the rainy and dry seasons, respectively, where the symbols circle, triangle, square, hexagon, diamond, asterisk, star and cross represent the [Ca^{2+}-HCO_3^-], [Na^+-HCO_3^-], [Na^+-Cl^-], [Mg^{2+}-HCO_3^-], [Mg^{2+}-SO_4^{2-}], [Mg^{2+}-Cl^-], [Na^+-SO_4^{2-}] and [Ca^{2+}-Cl^-] types, respectively. As shown in **Fig. 3-3**, PCA has 5 water types during the dry season and 6 water types during the rainy season. HUA on the other hand, as shown in **Fig. 3-4**, has 6 and 5 water types during the dry and rainy seasons, respectively.

In PCA, the [Ca^{2+}-HCO_3^-] and [Mg^{2+}-HCO_3^-] types are generally observed in the upstream area of the delta. However, the [Na^+-Cl^-] type is widely distributed not only in the downstream area but also in the middle-stream, up until the southern portion of Hanoi. According to Tanabe et al. (2003), during the Holocene, the sea transgressed the flood plain as far inland as the present location of Hanoi. The transgression during the Holocene, induced by sea level rise, must have caused an intrusion of seawater into the underlying high-permeability Pleistocene sediments. This may explain the reason for the [Na^+-Cl^-] type observed up until the southern portion of Hanoi. The [Na^+-HCO_3^-] type is observed dispersedly in the delta, which may be attributed to the depletion of Ca^{2+}, which is probably caused by cation exchange. This process is associated with saltwater intrusion in coastal aquifers or agricultural return flow that causes leaching of soluble salts in the agricultural areas. The [Na^+-SO_4^{2-}] type is found in the middle- stream area, which probably resulted from the dissolution of sulfate minerals (gypsum and anhydrite) commonly found in the

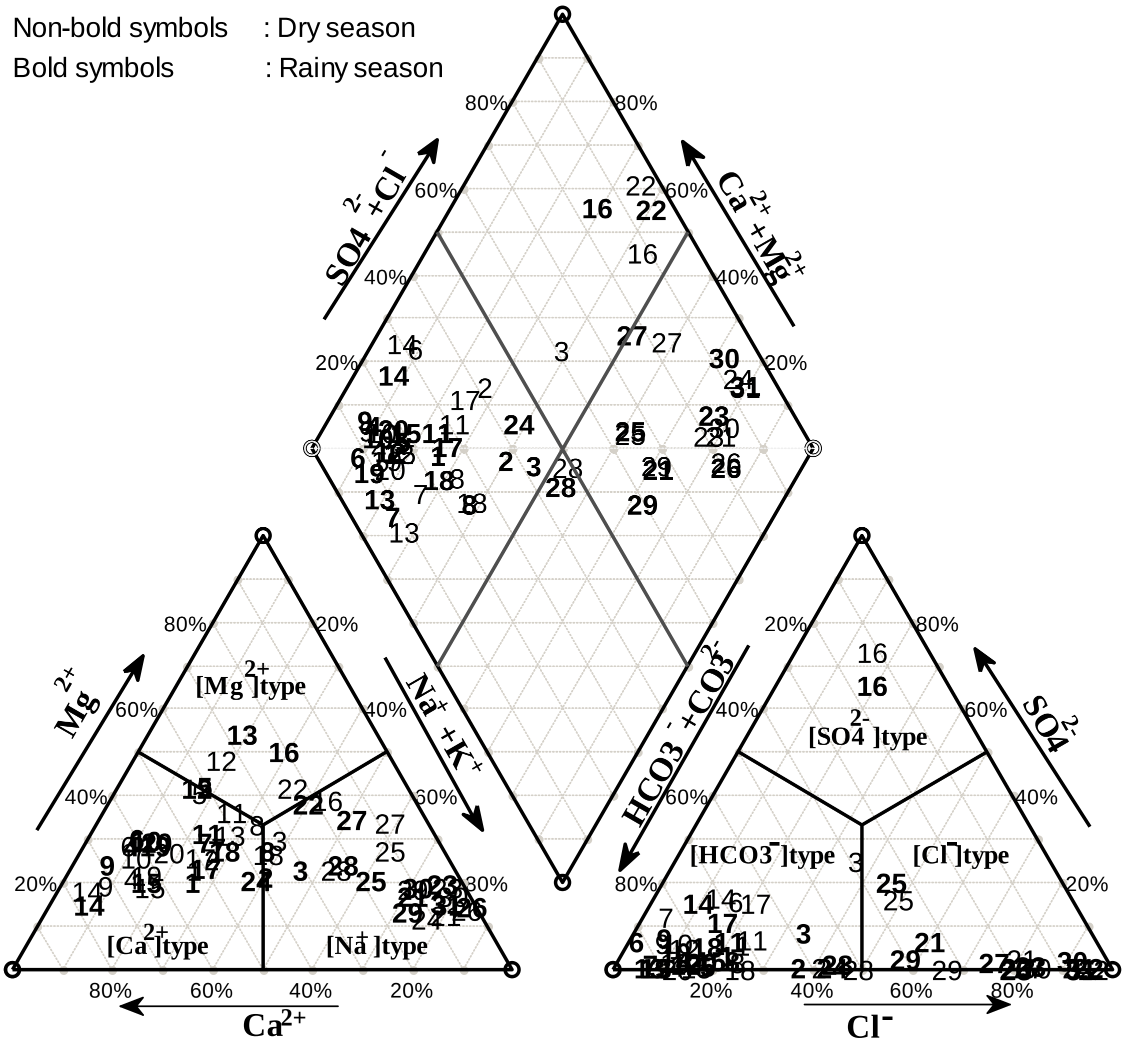

Fig. 3-2 Piper diagram for Holocene unconfined groundwater in the RRD

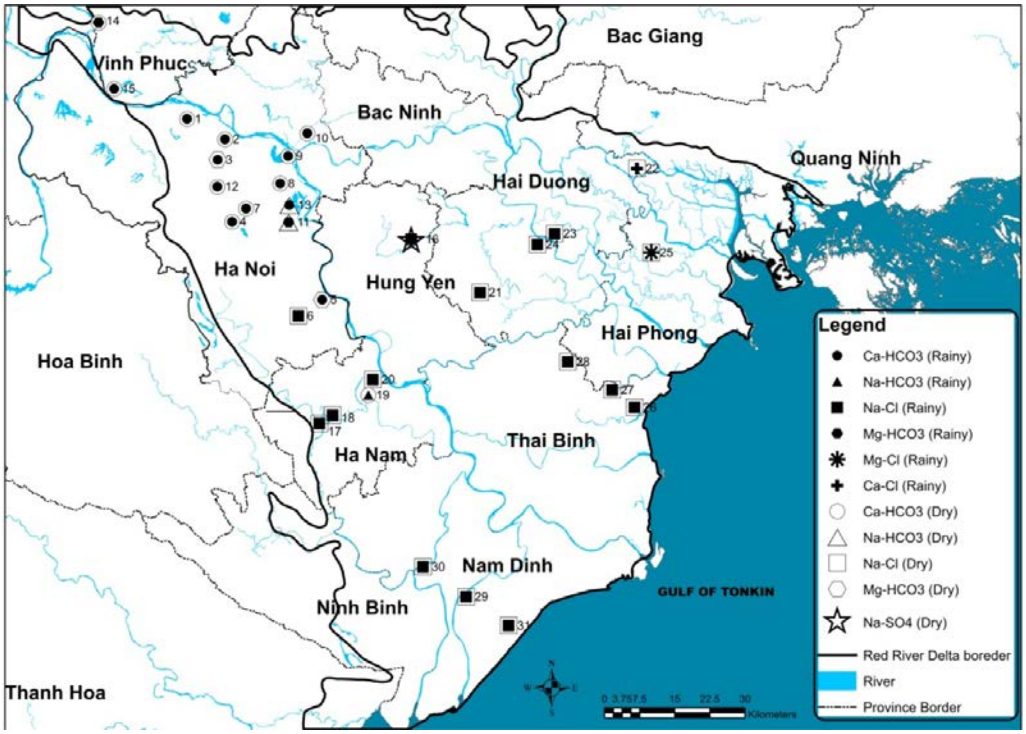

Fig. 3-3 Distribution of water type in Pleistocene confined aquifer

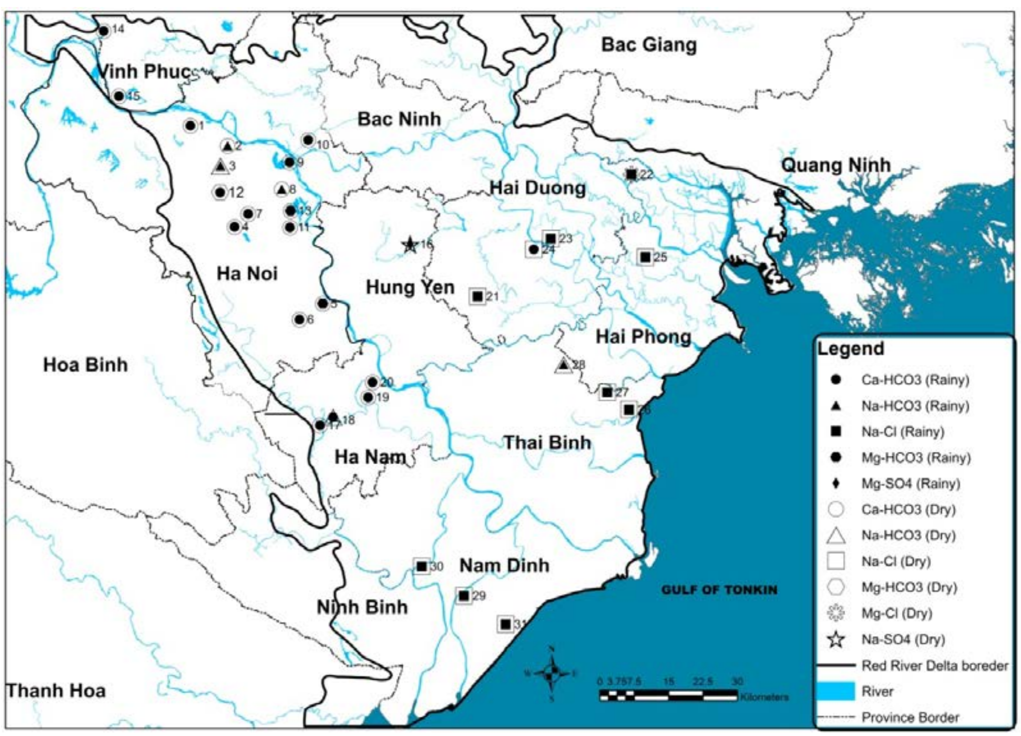

Fig. 3-4 Distribution of water type in Holocene unconfined aquifer

Quaternary aquifer system during its mixing with saltwater (El-Fiky, 2009). Other water types such as [Mg^{2+}-Cl^-] and [Ca^{2+}-Cl^-] are found in the Well Nos. 22 and 25 in the northeast part of the delta, which can be due to enrichment of Ca^{2+} and Mg^{2+} by dissolution of carbonate minerals in the aquifer system and/or depletion of Na^+ caused by cation exchange during its mixing with saltwater.

In HUA, similar to HUA, the [Ca^{2+}-HCO_3^-] and [Mg^{2+}-HCO_3^-] types, typical of fresh water were generally observed for both seasons at the upstream area (Vinh Phuc, Hanoi) and at the southwest middle-stream area of the delta (Ha Nam provinces). This indicates that fresh water is more widespread in the area along the right side bank of the Red River. According to Tran et al. (2012), the extent of the fresh groundwater zone in the HUA is geologically controlled by the extent of the Holocene marine transgression and the saltwater leaching mechanism in these sediments. The [Na^+-Cl^-] type, typical of saline water is found not only in the downstream area (Hai Phong, Thai Binh, Nam Dinh, Ninh Binh provinces) but also in the northeast middle-stream area (Hai Duong province) as shown in **Fig. 3-4**. Along the Red River and its tributaries, salty bottom water is transported as far inland as 35 km from the sea (Vu, 1996). This salty bottom water may leak into adjacent aquifers, either as a density-driven flow or as a downward flow controlled by a hydraulic gradient, where the river bottom sediments are highly permeable. Therefore, the predomination of the [Na^+-Cl^-] type in HUA in the downstream area is probably due to salt water intrusion from the river. The studies of Tanabe et al. (2006) and Tran et al. (2012) reveal that the ancient valley in the middle-stream area on the left side bank of the present Red River was filled up with marine sediments during the Holocene and the salty porewater may still be present in that area. Thus, the presence of the [Na^+-Cl^-] type in the northern middle-stream area could be influenced by salty paleowater.

To examine the differences between the two aquifers, the hydrogeochemical facies of all observation wells in **Figs. 3-1** and **3-2** are summarized and tabulated in **Table 3-3**. In this table the differences between the two aquifers are expressed by bold letters. In total, 11 and 17 out of the 31 observation wells during the dry and rainy seasons, respectively

Table 3-3 Water types of groundwater samples in HUA and PCA

Well Nos	HUA		PCA	
	Dry	Rainy	Dry	Rainy
1	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
2	[Ca^{2+}-HCO_3^-]	[Na^+-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
3	[Na^+-HCO_3^-]	[Na^+-HCO_3^-]	[Mg^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
4	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
5	[Ca^{2+}-HCO_3^-]	[Mg^{2+}-HCO_3^-]	[Mg^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
6	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
7	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
8	[Ca^{2+}-HCO_3^-]	[Na^+-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
9	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
10	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
11	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Na^+-HCO_3^-]	[Mg^{2+}-HCO_3^-]
12	[Mg^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
13	[Ca^{2+}-HCO_3^-]	[Mg^{2+}-HCO_3^-]	[Na^+-HCO_3^-]	[Ca^{2+}-HCO_3^-]
14	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Mg^{2+}-HCO_3^-]
15	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
16	[Na^+-SO_4^{2-}]	[Mg^{2+}-SO_4^{2-}]	[Na^+-SO_4^{2-}]	[Na^+-Cl^-]
17	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
18	[Na^+-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
19	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Na^+-HCO_3^-]
20	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
21	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
22	[Mg^{2+}-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]	[Ca^{2+}-Cl^-]
23	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
24	[Na^+-Cl^-]	[Ca^{2+}-HCO_3^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
25	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]	[Mg^{2+}-Cl^-]
26	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
27	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
28	[Na^+-HCO_3^-]	[Na^+-HCO_3^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
29	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
30	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
31	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]	[Na^+-Cl^-]

exhibited differences in the water type between the two aquifers. For instance, in the upstream area, the water in HUA Well No. 3 was of [Na^+-HCO_3^-] type during the dry season, but concurrently of the [Mg^{2+}-HCO_3^-] type in PCA Well No.3. This perhaps can be due to the materials that make up the two aquifers, and the interactions of the groundwater with the surface water and between the two aquifers. Interestingly, in both seasons, the water of HUA in Well No.6 was of the [Ca^{2+}-HCO_3^-] type, while PCA had the [Na^+-Cl^-] type. In the middle-stream area, the water samples of HUA in Well Nos. 17, 18, 20 and 24 were of the [Ca^{2+}-HCO_3^-] type during the rainy season, while PCA had the [Na^+-Cl^-] type. These differences between HUA and PCA are probably due to leaching of paleowater from marine sediments. In the RRD, the sea-level change from 20,000 to 8,000 years ago must have been the overall controlling mechanism of the distribution of fresh and salty groundwater in the Red River plain aquifers (Tran et al., 2012).

Seasonal changes in the hydrogeochemical facies can also be observed in **Table 3-3**, which are indicated by hatched cells. In PCA, there are 9 out of the 31 observation wells that show changes in the water type from the dry to the rainy seasons. Similar to HUA, 8 out of the 9 wells showed changes in the cation type: from [Mg^{2+}] to [Ca^{2+}], from [Na^+] to [Ca^{2+}] or [Mg^{2+}], or from [Ca^{2+}] to [Mg^{2+}] or [Na^+]. However, there is only one observation well (PCA Well No.16) that showed change in the anion type (from the [SO_4^{2-}] to [Cl^-] type). These changes imply that water infiltration from HUA may affect the concentrations of chemical constituents of the PCA groundwater during the rainy season through hydrogeological windows, where the aquitard sandwiched by the two aquifers is completely missing.

For HUA, 9 out of the 31 observation wells exhibited seasonal changes in terms of the cation water type. For example, HUA samples from Well Nos. 5 and 13 changed from the [Ca^{2+}] to [Mg^{2+}] type, and Well Nos. 2 and 8 changed from the [Ca^{2+}] to [Na^+] type. More interestingly, the water type in HUA Well No.24 changed in both cation and anion (from the [Na^+-Cl^-] to [Ca^{2+}-HCO_3^-] type). These changes suggest that surface water may have strong influence on HUA groundwater at the upstream and middle-stream areas of the delta, but weakly influences the downstream area during the rainy season.

3.3.3 Factors governing water chemistry

The soluble ions in natural waters mainly come from the rock and soil weathering, anthropogenic input and partly from the atmosphere input (Xing et al., 2013). Gibbs diagram could be used to analyze the genesis mechanisms of water chemistry (Mamatha and Sudhakar, 2010). **Fig. 3-5** shows the Gibbs diagram for groundwater in PCA. Gibbs (1970) found that most of the world's surface water falls within the "boomerang"-shaped boundaries. In this study, these boundaries are labeled as boundary G^+ in the Gibbs cation diagram (**Fig. 3-5a**) and boundary G^- in the Gibbs anion diagram (**Fig. 3-5b**). On the basis of analytical chemical data for numerous surface samples, Gibbs theorized the three major mechanisms controlling world surface water chemistry which are presented in three domains: precipitation dominance, rock dominance and evaporation dominance as shown in **Fig. 3-5**. The boundaries between these domains, however, were not clearly defined. According to Kumar (2009), for groundwater, the domain of rock dominance extends further towards higher weight ratios as shown by the elongated boundaries, which in this study are presented by the boundaries as K^+ (**Fig. 3-5a**) and K^- (**Fig. 3-5b**), respectively. This relatively new perspective on Gibbs diagram was also adopted by other researches (e.g. Ravikumar et al., 2011, Raju et al., 2011, Gurugnanam et al., 2009) in order to clearly delineate the 3 domains of the natural mechanisms. Utilizing the symbol convention used in **Figs. 3-1** and **3-2**, the number symbols in **Fig. 3-5** correspond to the locations of the observation wells in **Fig. 2-3**. The non-bold and bold symbols indicate the dry and rainy season data, respectively.

As shown in **Fig. 3-5**, almost all of samples (from Well Nos. 1 to 15) in both seasons located in the upstream area, except the samples from Well No. 6, fall inside G^+, G^- and K^+, K^- boundaries with extremely low weight ratio Cl/(Cl+HCO3) (less than 0.1 as shown in **Fig. 3-5b**). This is consistent with the Piper diagram for PCA (**Fig. 3-2**), where the [HCO_3^-] type is exceedingly dominant in the PCA groundwater of the upstream area. The Pleistocene aquifer in the RRD is recharged mainly by the surrounding mountain range,

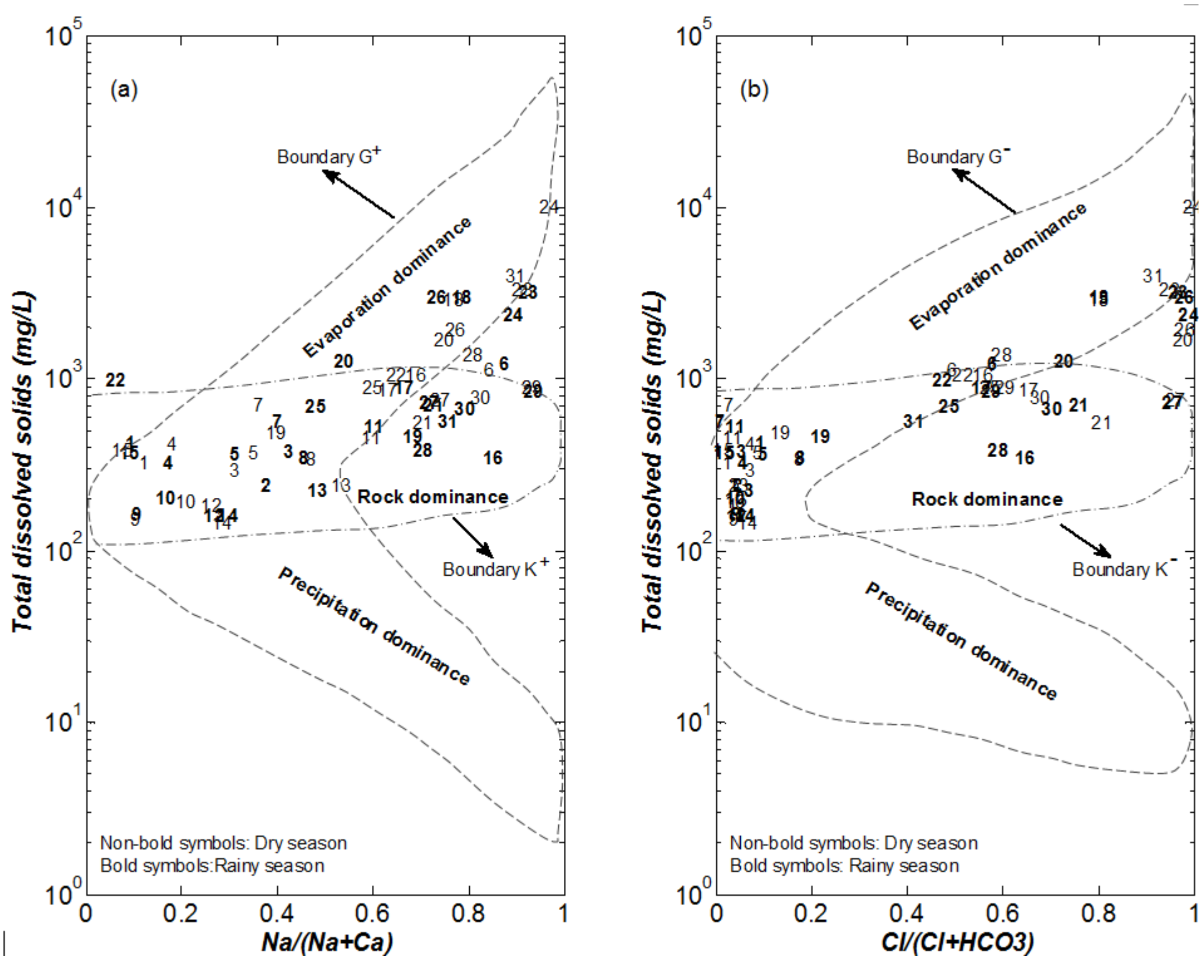

Fig. 3-5 Gibbs diagram for Pleistocene confined groundwater in the RRD

which is carbonate rock formations consisting of marble, limestone and dolomite (Tran et al., 2012, Drogue et al., 2000). This suggests that in the upstream area, the PCA groundwater chemistry is controlled by the dissolution of carbonate minerals, whereas the HUA groundwater composition is affected by both the dissolution of carbonate minerals and surface water. **Fig. 3-6** also shows that the PCA groundwater samples in the middle-stream area from Well Nos. 16,17,19 and 21 have relatively high weight ratios Na/(Na+Ca) and Cl/(Cl+HCO3), but low TDS and thus fall inside the K^+, K^- boundaries. This suggests that rock-water interaction is the controlling factor of the groundwater chemistry in the areas along these wells. Note that PCA samples from Well Nos. 23, 24 (in the northeast middle-stream area), and 26 (in the downstream area) show very high weight ratios for Na/(Na+Ca) and Cl/(Cl+HCO3) (reaching to almost a value of 1.0) as well as very high TDS. This suggests that the main source of the dissolved solids in the PCA groundwater in this area is oceanic porewater from marine sediments. Interestingly, the PCA groundwater samples in Well Nos. 29, 30, and 31 (located in Nam Dinh province - the southern downstream area) (except the dry season sample in Well No. 31) have relatively high ratios Na/(Na+Ca) and Cl/(Cl+HCO3) but low TDS and thus fall inside the K^+, K^- boundaries. This reveals that salt water intrusion is prevented by groundwater recharge, which makes rock-water interaction become the dominant factor that controls the groundwater chemistry along this coastal area. Wagner et al. (2012) identified a local lens of low saline pore water in the Pleistocene aquifer in Nam Dinh province, which are regionally known to contain brackish and saline pore waters affected by salt water intrusion. The reason for this phenomenon is that the constant influx of fresh groundwater from adjacent Triassic hard rocks results in flushing of the primary Pleistocene pore water and preventing the infiltration of saline water from marine Holocene sediments (Wagner et al., 2012). Therefore, the presence of freshwater lens would be the reason that groundwater samples in the southwestern part of the downstream areas fall in the rock dominance domain (**Fig. 3-6**). In addition, similar to the RRD, the phenomenon of freshwater lens was also reported in other deltas such as the Niger Delta in Nigeria (Oteri and Atolagbe, 2003), the Nile Delta in Egypt (Kashef, 1983), the Dibdibba Delta in Iraq (UN-ESCWA and BGR, 2013).

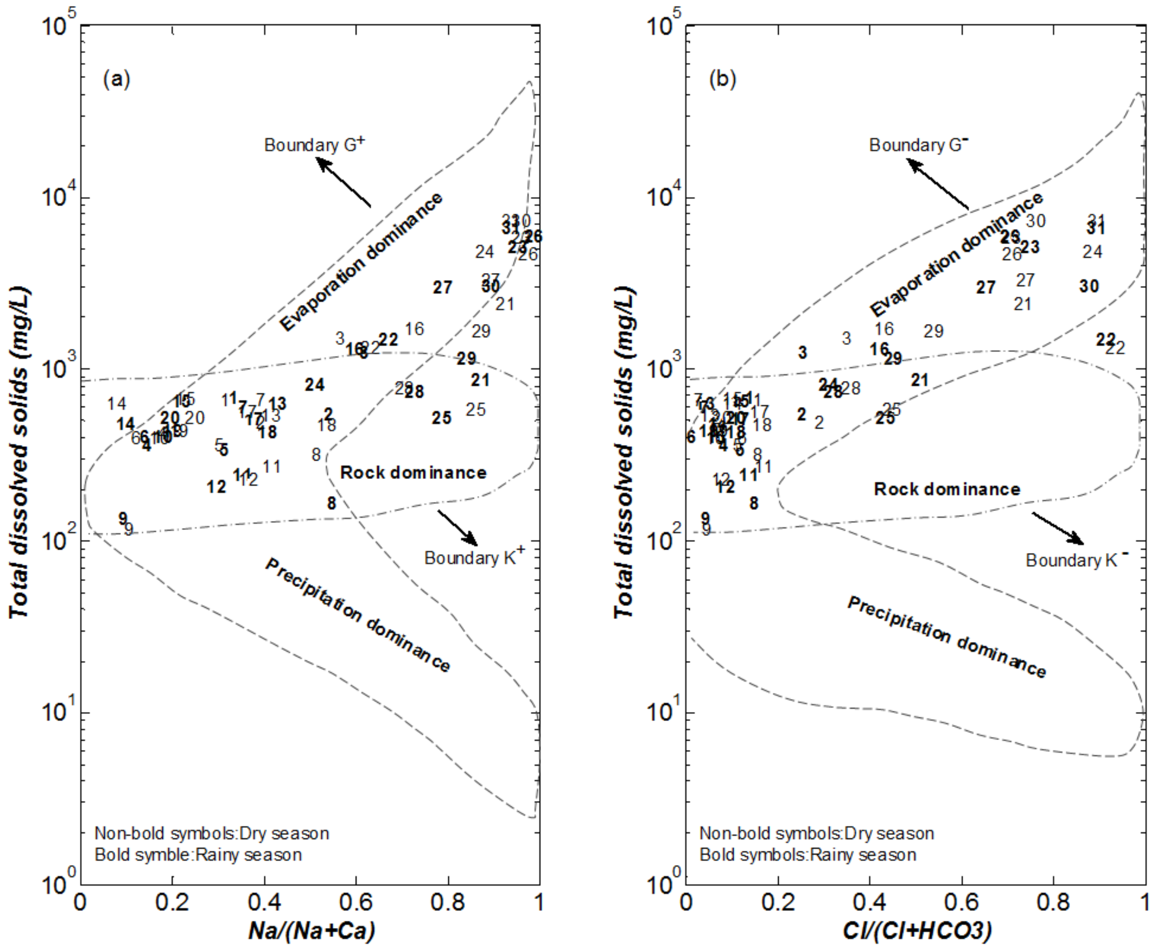

Fig. 3-6 Gibbs diagrams for Holocene unconfined groundwater in the RRD

Concerning the change from the dry to rainy season, it is also observed that some PCA groundwater samples show conspicuous changes in Na/(Na+Ca), Cl/(Cl+HCO3) and TDS between the dry and rainy seasons, such as for samples coming from Well Nos. 20, 24, 28 and 31. These PCA samples also tend to fall closer on the domain of rock dominance in the rainy season. This may be due to three factors: 1) increased exploitation of PCA groundwater during the dry season resulting in leaching saltwater from the adjacent aquifer; 2) increased recharge during the rainy season and 3) saltwater intrusion coming from the sea.

To determine the source of the dissolved chemical components in the HUA groundwater, the Gibbs diagram was also created as shown in **Fig. 3-6**. Similar to PCA, almost all HUA groundwater samples in both seasons from Well Nos. 1 to 15, which are located in the upstream area as shown in **Fig. 2-4**, fall inside not only within the boundaries G^+ and G^- but also within the K^+ and K^- boundaries. This suggests that rock-water interaction is the major source for dissolved ions in the upstream area of the delta. Groundwater samples in the southern portion of the middle area (from Well Nos. 17 to 20), also fall inside the G^+, G^- and K^+, K^- boundaries. This suggests that rock-water interaction is also the natural mechanism controlling the dissolved ions in groundwater at the southwest portion of the middle-stream area of the delta. However, samples in the northeast part of the middle-stream area (Well Nos. 16, 21 to 24) fall outside K^+, K^- boundaries except the sample from Well No. 21 in the rainy season, indicating the dominant evaporation influence on the water chemistry. In the downstream area, almost all the samples (Well Nos. 25 to 31) fall outside the K^+ and K^- boundaries and toward the domain of evaporation dominance, except for HUA Well No. 25 and 28, which implies that salt water intrusion is the main factor affecting the groundwater in the downstream area.

Regarding the change from the dry to the rainy season, almost all samples in HUA show no significant changes in TDS and in the weight ratios Na/(Na+Ca), Cl/(Cl+HCO3). Some samples, such as Well Nos. 21 and 24, which are located near the river in the northern middle of the RRD (shown in **Fig. 2-4**), present remarkable decrease in TDS and in the weight ratio Cl/(Cl+HCO3). In other words, these samples moved from the domain of evaporation dominance in the dry season, to the rock dominance in the rainy season. The increase of groundwater recharge from the surface water (river) and infiltration of rainfall during the rainy season causes dilution of groundwater ion concentration, which could explain the change in domains of some of the water samples.

The differences in groundwater chemistry between PCA and HUA are also observed by comparing **Fig. 3-5** to **Fig. 3-6**. Two HUA groundwater samples from Well No. 3 show high TDS and high weight ratios Na/(Na+Ca) and Cl/(Cl+HCO3) compare to other samples in the upstream area, and thus fall in evaporation dominance area, whereas with the same location, two PCA dry and rainy samples from Well No. 3 have lower weight ratios Na/(Na+Ca) (less than 0.4) and Cl/(Cl+HCO3) (less than 0.1) as well as low TDS (about 300 mg/L) and thus, fall in the domain of rock dominance. By closer inspection of the land use, this well is located in an agricultural area of intensive irrigation (Dijk et al., 2012). In addition, the irrigation and drainage systems have problems such as inadequate capacity, inadequate grade, and absence of (or ineffective) water control structures, accompanied by rapid increases in canal seepage (Asian Development Bank, 2000). Thus it is reasonable to infer that agricultural activities may have caused the HUA groundwater samples of Well No. 3 to fall inside the domain of evaporation dominance. This however, does not yet affect the groundwater in the PCA aquifer. Another noteworthy point emerging from the Gibbs diagrams for HUA and PCA (**Figs. 3-5** and **3-6**) is that the HUA groundwater samples from Well Nos. 6 (southern of Hanoi), 17, 18 and 20 (Ha Nam province as shown in **Fig. 2-4**), which are located in the middle area of the delta have low weight ratios Na/(Na+Ca) and Cl/(Cl+HCO3) as well as TDS, whereas the PCA groundwater samples at the same locations have very high weight ratios Na/(Na+Ca) and Cl/(Cl+HCO3), and TDS. This suggests that vertical diffusion of saline pore water in shallow Holocene sediments would be a source for high saline groundwater in deeper aquifers (PCA), whereas the HUA groundwater is affected by rainfall and surface water.

3.6 Conclusion

The main objectives of this study are to investigate the changes in hydrogeochemical characteristics of groundwater from the dry to the rainy seasons and their spatial distribution in the two main aquifers of the RRD, Vietnam. In this paper, hydrogeochemical parameters from 31 conjunctive sampling wells for HUA and PCA in the RRD acquired during the dry and the rainy seasons in 2011 were comprehensively analyzed. Interpretation of the hydrogeochemical analyses revealed that the concentrations of most ions are higher in HUA than in PCA throughout the year. The concentrations of almost all of the ions decrease from the dry season to the rainy season in both aquifers.

In terms of hydrogeochemical facies, from the analysis of Piper diagrams for HUA and PCA, the following generalizations were obtained as groundwater properties in the RRD: the [Ca^{2+}-HCO_3^-] type groundwater is quite abundant in the upstream area of the delta, while the [Na^+-Cl^-] type is dominated in the downstream area. Changes in the hydrogeochemical facies were detected from the dry to the rainy seasons in approximately one third of the sampling wells in both aquifers. The change particularly occurs in the cation type (i.e., [Ca^{2+}] to [Mg^{2+}] or [Na^+], [Mg^{2+}] to [Ca^{2+}], [Na^+] to [Ca^{2+}] or [Mg^{2+}]), whereas the anion type remains almost unchanged. Most of them are observed in the upstream area of the delta. Differences in the hydrogeochemical facies between HUA and PCA were also observed in about 45% of the observation wells. These differences are observed mostly in the upstream and middle-stream areas of the delta.

The Gibbs diagram suggests that in HUA, the natural mechanism controlling groundwater chemistry is the rock-water interaction in the upstream and southwest middle-stream areas, while marine activities, such as salty paleowater and salt water intrusion, affect groundwater chemistry in the rest of the delta. In PCA, the source of the dissolved ions in the groundwater is rock-water interaction in the upstream and the southeast downstream area, but salty paleowater and salt water from the sea are the main factors influencing groundwater chemistry in the middle-stream and northern downstream areas. The findings of this study provide valuable information regarding the groundwater hydrogeochemical properties and hydrodynamics in the RRD, Vietnam.

In this study, the Piper and Gibbs diagrams were used for different purposed. The Piper diagram was used to classify the major ions in the groundwater into various hydrogeochemical types to investigate and identify the hydrogeochemical facies, while Gibb diagram was employed to assess the functional sources of dissolved chemical constituents of groundwater. Seasonal changes in water type were detected by using the Piper diagram, but the Gibbs diagram showed no significant changes in the natural mechanism controlling groundwater chemistry in the RRD. In other words, the Piper diagram showed more sensitivity of the seasonal changes than the Gibb diagram. While the Piper diagram demonstrated the water types showing the essential chemical characters of different constituents in percentage values, the Gibbs diagram consider TDS of groundwater, which is a very important factor in groundwater quality assessment. Therefore, simultaneously using the Piper and Gibbs diagrams will further the insightful understanding of hydrogeochemical characteristics of groundwater in the RRD.

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CHAPTER 4

ASSESSMENT OF SPATIO-SEASONAL HYDROGEOCHEMICAL CHARACTERISTICS OF GROUNDWATER USING SELF-ORGANIZING MAPS

4.1 Introduction

Clustering is an unsupervised method of data grouping using a given measure of similarity. Clustering algorithms attempt to organize unlabeled feature vectors into clusters (natural groups) such that samples within a cluster are similar to each other but differ from those in other clusters (Hilario et al., 2004). Clustering analysis is an important and useful tool for analyzing large datasets that contain many variables and experimental units. Therefore, the application of cluster analysis to complex datasets has attracted a high level of scientific interest in various aspects of water research, such as surface water (Hall and Minns, 1999), rainfall (Astel et al., 2004), and water quality (Alberto et al., 2001; Vialle et al., 2011).

In hydrogeochemical studies, cluster analysis serves the purpose of isolating a group of representative clusters (also known as water type or hydrogeochemical facies) that reflect the processes generating the natural variability found in hydrogeochemical parameters. These representative clusters, which help define the major chemical trends, can provide insight into aquifer heterogeneity and connectivity, as well as the physical and chemical processes controlling water chemistry (Güler and Thyne, 2004). A number of studies have been published during the past few decades that investigate hydrogeochemical characteristics of groundwater by applying cluster analysis, e.g., from Europe (Lambrakis et al., 2004), Africa (Belkhiri et al., 2011; Hussein, 2004), and Asia (Zhang et al., 2012; Reghunath et al., 2002). The focus of this study is the RRD (RRD) in Vietnam, where undue groundwater exploitation without the wise management and adequate understanding of hydrogeochemical characteristics have caused serious problems, such as decline of groundwater level, land subsidence, and groundwater pollution (Bui et al., 2011).

The RRD is the second largest delta in Vietnam with an area of about 13,000 km^2 and a population of around 20 million people in 2012 (23% of Vietnam's total population), which makes it one of Vietnam's most densely populated regions (Vietnam General Statistic Office, 2013). All its residents depend entirely on groundwater for their domestic water supply. Due to the importance of groundwater in the RRD as well as the region's importance in the development of Vietnam, in recent years several studies on groundwater have been carried out. For example, Tran et al. (2012) investigated the origin and extent of fresh groundwater, salty paleowaters, and saltwater from recent seawater intrusions in the RRD using geological observations, geophysical borehole logging, and transient electromagnetic methods. Arsenic pollution of groundwater in the entire RRD has been studied by Winkel et al. (2011) on the basis of a complete geo-referenced database with 37 chemical parameters from several hundred wells. In our earlier studies, we investigated the spatial characteristics of the aquifer system (Bui et al., 2011) as well as groundwater level trends in the entire RRD (Bui et al., 2012). To date, there has not been any published study that focuses on the hydrogeochemical characteristics of the groundwater in the RRD on the basis of major ion chemistry, which is fundamental and among the key considerations to comprehensively understand the hydrogeochemical processes that influence the nature and chemistry of groundwater.

Groundwater interacts with surface hydrologic systems, such as rivers, lakes, and oceans, and is indirectly influenced by seasonal changes during recharge and discharge. The change in seasons can potentially affect the hydrogeochemical properties of groundwater, especially in areas that have distinct dry and rainy seasons, like Vietnam. The hydrogeochemical characteristics in the RRD can also be affected by the change in seasons; hence, investigation of the changes in the hydrogeochemical properties from the dry to the rainy seasons (or vice versa) may reflect the groundwater hydrodynamics and circulation. It may also help improve the data collection programs for groundwater assessment and enable better use of groundwater supplies. However, there have been no studies regarding the changes in the hydrogeochemical properties during the dry and rainy seasons in the RRD.

In order to investigate the spatial–seasonal hydrogeochemical characteristics of groundwater, it is essential for a robust classification scheme to cluster water chemistry samples into homogeneous groups (Güler and Thyne, 2004). Several common clustering techniques have been utilized to divide groundwater samples into similar homogeneous groups (each representing a hydrogeochemical facies) with the ultimate objective of characterizing the quality of groundwater. For example, Belkhiri et al. (2011) adopted principal component analysis and Q-mode hierarchical cluster analysis to assess the chemistry of groundwater and identify the geological factors that affect the water chemistry in the east of Algeria. Güler and Thyne (2004) applied the fuzzy c-means clustering technique to a large hydrochemical dataset from the Indian Wells-Owens Valley area of southeastern California to delineate clusters of water samples with similar characteristics. Reghunath et al. (2002) applied Q- and R-mode factor and cluster analysis to improve the understanding of groundwater systems in Karnataka, India. These methods are efficient at grouping water samples by chemical similarities, but are not useful for the visual assessment of the results and presentation of maps showing hydrogeochemical facies (Güler et al., 2002). The recently proposed method of the self-organizing maps (SOM) is likely to become a complementary or alternative tool to the clustering methods (Kaltel et al., 2008; Iseri et al., 2009).

The SOM is based on an unsupervised learning algorithm, and has excellent visualization capabilities, including techniques that use the reference vectors of the SOM to give an informative picture of the data (Hong et al., 2003). The SOM has been implemented in various aspects of water research, e.g., classification of environmental monitoring data (Jin et al., 2011) and clustering for wastewater treatment monitoring (Hilario et al., 2004). The SOM has also proven to be a powerful and effective data analysis tool in meteorological analysis and detection of long-term changes in climate (Nishiyama et al., 2007; Leloup et al., 2007). However, the SOM has not yet been systematically applied for the classification of groundwater quality samples in order to investigate hydrogeochemical characteristics. This study is the first attempt to apply the SOM in combination with a hierarchical cluster analysis for clustering hydrogeochemical groundwater data.

Through the initiative of the national government (National Hydrogeological Database Project), hydrogeochemical data in the RRD were collected from the 52 Pleistocene confined aquifer (PCA) wells and the 47 Holocene unconfined aquifer (HUA) wells in 2011 during the dry and rainy seasons. The objective of this study is to cluster spatial–seasonal hydrogeochemical data to assess the groundwater quality of the two main aquifers in the RRD using SOM and Gibbs diagram. In this study, Gibbs diagram was aptly used to elucidate the cause and significance of the hydrogeochemical characteristics clustered by the SOM. Gibbs (1970) proposed chemical diagrams for the assessment of functional sources of dissolved chemical constituents and for inferring the mechanism controlling the chemistry of surface water. Various researchers have already demonstrated the usefulness of Gibbs diagram for groundwater (Raju et al., 2011; Marghade et al., 2012; Yidana et al., 2010). The findings from this study will provide valuable insights into the spatial–seasonal hydrogeochemical characteristics of groundwater in the RRD.

4.2 Methodology

The SOM, developed by Kohonen (2001), is one kind of artificial neural network that is characterized by unsupervised training. It can project high-dimensional, complex target data onto a two-dimensional, regularly arranged map in proportion to the degree of similarity (Jin et al., 2011). In other words, the SOM accomplishes two objectives simultaneously: reducing dimensions and displaying similarities. Therefore, it is an effective tool to visualize and explore data properties. In general, the objective of the SOM application is to obtain useful and informative reference vectors (also referred to as weight vectors, prototype vectors, and codebook vectors) (Hilario et al., 2004). These vectors can be acquired after iterative updates through the training of the SOM, which is composed of three main procedures: competition between nodes, selection of a winner node, and update of the reference vector of each node.

Standardization of the data was necessary prior to the application of the SOM to ensure that all values of the chemical parameters were given the same or similar importance The results of the SOM application were sensitive to the data pre-processing method used, as the SOM is trained to be organized according to the Euclidean distances between input data (Jin et al., 2011). In this study, standardization of the data is carried out by scaling the variable values between [0,1] with a simple linear transformation, as shown in Eq. 4-1:

$$x'_{ij} = \frac{x_{ij} - \min(x_j)}{\max(x_j) - \min(x_j)} \qquad (4-1)$$

where x_{ij} is the concentration values of the chemical parameters of the i^{th} wells.

Design of the SOM structure (calculation of the total number of nodes, side lengths), selection of a proper initialization method, and data transformation methods are very important features in the SOM application. The number of map nodes determines the accuracy and generalization capability of the SOM. According to the properties of the SOM, the bigger the map size is, the higher the resolution for pattern recognition, while the topographical adjacency is further among the clusters. A reasonable optimum solution of the compromise among the accuracy of pattern classification and topographical proximity of clusters to determine the number of the SOM nodes is the heuristic rule, as shown in Eq. 4-2:

$$m = 5\sqrt{n} \qquad (4-2)$$

where, m denots the number of the SOM nodes and n represents the number of input data (Vesanto et al., 2000; Jeong et al., 2010; Hentati et al., 2010; Jin et al., 2011). In this study, this heuristic formula was used to determine the total number of nodes in the SOM. The ratio of the number of rows and columns was calculated by the square root of the ratio between the two biggest eigenvalues of the transformed data, as shown in Eq. 4-3 (Hilario et al., 2004).

$$\frac{n_1}{n_2} = \sqrt{\frac{e_1}{e_2}} \qquad (4-3)$$

where, n_1, n_2 are the number of rows and column of the SOM maps, respectively, and e_1, e_2 are the two biggest eigenvalues of the transformed data.

After establishing the SOM structure, reference vectors for the SOM with the commonly used hexagonal array are initially set using the linear initialization method. In this study, due to limited data, the linear initialization method was used, as it is more suitable for the pattern classification than the random initialization. The random initialization requires a large dataset and might cause boundary effects near the edges of the map (Vesanto et al., 2000; Hentati et al., 2010; Jin et al., 2011). In addition, the linear initialization approach can use eigenvalues and eigen vectors of the input data to set the initial reference vectors on the structured SOM. This means that the initial reference vectors already include prior information about the input data, resulting in an acceleration of the training phase (Vesanto et al., 2000; Jin et al., 2011). In this study, each reference vector was updated through the SOM training process using the batch mode, as shown in Eq. 4-4:

$$m_i(t+1) = \frac{\sum_{j=1}^{n} h_{ic}(t)x_j}{\sum_{j=1}^{n} h_{ic}(t)} \qquad (4-4)$$

$$c = \text{argmin}_k\{\|x_j - m_k\|\} \qquad (4-5)$$

where, c is index of the BMU of data samples x_j and h_{ic} (t) is the weight of each data sample using the neighborhood function value- Gaussian, as shown in Eq. 4-6:

$$h_{ci}(t) = e^{\frac{-d_{ci}^2}{2\sigma_t^2}} \qquad (4-6)$$

The reference vectors obtained at the end of the training process can be fine-tuned using cluster analysis methods. Various clustering algorithms are available in literature. These algorithms are generally classified into two types: hierarchical clustering and partitional clustering. These two clustering types can be integrated such that a result given by a hierarchical method can be improved via a partitional step, which refines via iterative relocation of points (Hilario et al., 2004). In this study, both clustering algorithms were applied for the fine-tuning of the reference vectors. For the partitional clustering methods, the k-means algorithm is the most frequently used method for the SOM (Jin et al., 2011, Hentati et al., 2010; Nishiyama et al., 2007; Hilario et al., 2004). The optimal number of clusters was selected by the Davies–Bouldin index (DBI) using the k-means algorithm, as shown in Eq. 4-7:

$$\mathrm{DBI} = \frac{1}{N}\sum_{i=1, i\neq j}^{N} \max\left(\frac{\sigma_i + \sigma_j}{d(c_i, c_j)}\right) \qquad (4-7)$$

Where, σ is standard deviation, N is number of clusters; σ_I, σ_j are the average distance of all patterns in cluster i,j to their cluster center c_I, c_j, respectively; and $d(c_i, c_j)$ is the distance of cluster centers c_I and c_j. The DBI values were calculated from a minimum of 2 clusters to the total number of nodes. The calculation was based on the "similarity within a cluster" and "dissimilarity between clusters." Therefore, the number of clusters showing the minimum DBI was optimal for the trained SOM (Hilario et al., 2004; Nishiyama et al., 2007). For the hierarchical method, Ward's linkage method is the most commonly used approach (Jin et al., 2011; Hentati et al., 2010). In this study, a final fine-tuning cluster analysis was carried out by Ward's method using the optimal number of clusters.

To investigate the mechanisms governing the groundwater chemistry of the RRD, the chemical diagrams that were proposed by Gibbs (1970) were used to further evaluate the clustered data from the PCA and HUA wells. The weight ratios Na/(Na+Ca) and Cl/(Cl+HCO_3) were plotted against the TDS separately on a logarithmic axis to represent the Gibbs cation and anion diagrams, respectively. The Gibbs diagram was originally used to evaluate surface waters, but recent groundwater quality studies have used these diagrams to assess the sources of dissolved chemical constituents of groundwater (Raju et al., 2011; Marghade et al., 2012; Yidana et al., 2010).

4.3 Results and discussion for PCA

4.3.1 SOM and clustering results

The input data for the SOM application were concentrations of 8 chemical parameters (major ions: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-}, Cl^{-} and CO_3^{2-}) of 104 samples, which were observed in 52 PCA wells during the dry and rainy seasons. Based on the methodology described above, the number of the SOM nodes was calculated as 56, and the numbers of rows and columns were 8 and 7, respectively. This SOM was used for the cluster analysis of the standardized groundwater chemistry monitoring data.

Fig. 4-1 shows the 8 component SOM maps finally obtained after the training process. Each map represents the component value of the reference vectors for the 56 SOM nodes, in which the reference vectors were standardized to range 0–1, using gradient of colors. The nodes that represent the high values are in red color and the low values are colored blue color. A comparison between the component SOM maps, by means of a gradient of color, can indicate informative and qualitative relations (or correlations) among the studied parameters. Through visual investigation of SOM maps in **Fig. 4-1**, Mg^{2+}, Na^{+}, K^{+}, and Cl^{-} have similar color gradients. This means that there is strong positive correlation among these 4 parameters. In contrast, CO_3^{2-} showed a negative correlation with these parameters by the inverse color gradient of the SOM maps. The component maps of HCO_3^{-} and SO_4^{2-} did not show any correlation with the other parameters, as can be seen in **Fig. 4-1**.

Table 4-1 shows the correlation coefficients among 8 physicochemical parameters using the standardized reference vectors. This table quantitatively confirms the strength of the relations between these parameters. For example, the relationship of Cl^{-} with Mg^{2+}, K^{+}, and Na^{+} indicated significantly high correlation coefficients, more than 0.95. CO_3^{2-} mainly showed an inverse correlation with the other parameters except for HCO_3^{-}, but the correlation coefficients were relatively low, as shown in **Table 4-1**.

In order to select the optimal number of clusters, the DBI values based on the k-means clustering algorithm were calculated for the minimum (2 clusters) to the maximum (56 clusters) number of possible clusters. **Fig. 4-2** shows the variation of the DBI values after being applied to the data and the front part between 2 and 20 clusters was magnified to show the minimum DBI visibly. The most appropriate number of clusters corresponding to

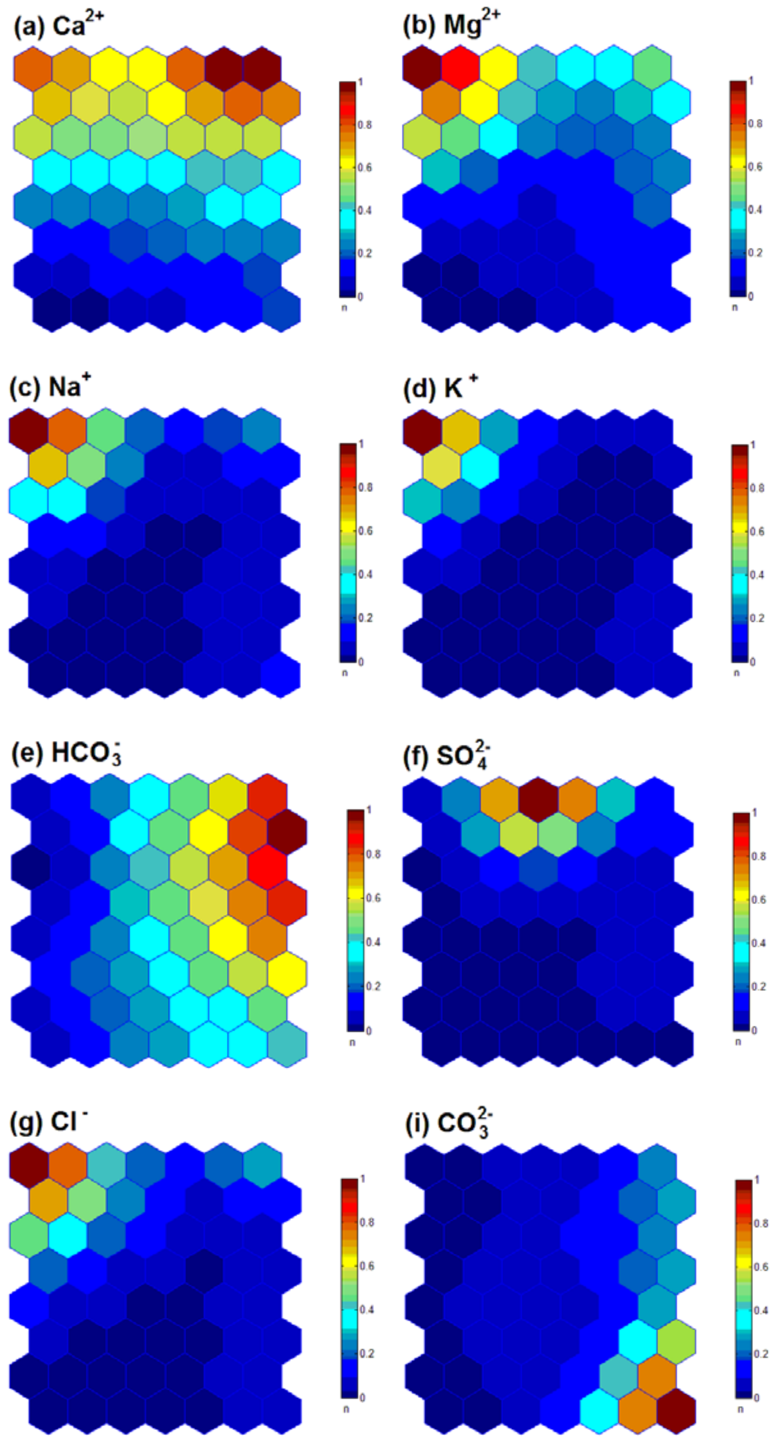

Fig. 4-1 Component planes for (a) Ca^{2+}, (b) Mg^{2+}, (c) Na^{+}, (d) K^{+}, (e) HCO_3^{-}, (f) SO_4^{2-}, (g) Cl^{-}, (i) CO_3^{2-}.

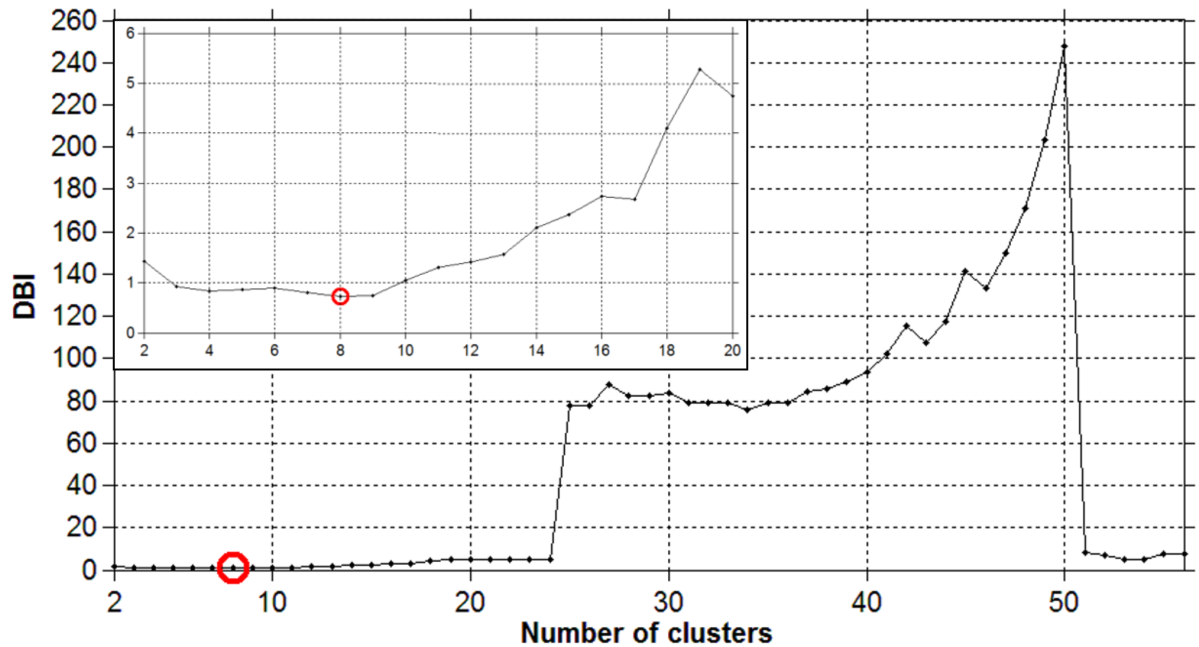

Fig. 4-2 Variation of DBI values with the optimal number of clusters marked by the circle on the figure**.**

Table 4-1 Correlation coefficients among 8 physicochemical parameters.

	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	HCO_3^{-}	SO_4^{2-}	Cl^{-}
Mg^{2+}	0.77						
K^{+}	0.43	0.88					
Na^{+}	0.56	0.95	0.98				
HCO_3^{-}	0.37	-0.09	-0.37	-0.30			
SO_4^{2-}	0.53	0.42	0.17	0.27	0.07		
Cl^{-}	0.59	0.96	0.97	0.99	-0.32	0.28	
CO_3^{2-}	-0.16	-0.19	-0.18	-0.18	0.44	-0.16	-0.23

the minimum DBI was 8. Once the optimum cluster number had been selected, the hierarchical clustering algorithm using Ward's method was carried out to obtain the 8 clusters for fine-tuning the pattern classification.

Fig. 4-3 shows the hierarchical cluster tree with the nodes of the SOM classified into 8 different clusters. The nodes in the SOM map are numbered from top to bottom and from left to right. As shown in this figure, Clusters 4 and 6 have the smallest distance or highest similarity between clusters. This means that Cluster 4 has similar hydrogeochemical characteristics to Cluster 6. In the same way, Clusters 1 and 3 have similar characteristics, as well as Clusters 5 and 8. In addition, Clusters 2 and 7 have higher similarity with Clusters 5 and 8 and Clusters 4 and 6, respectively, than the other clusters, as shown in **Fig. 4-3**.

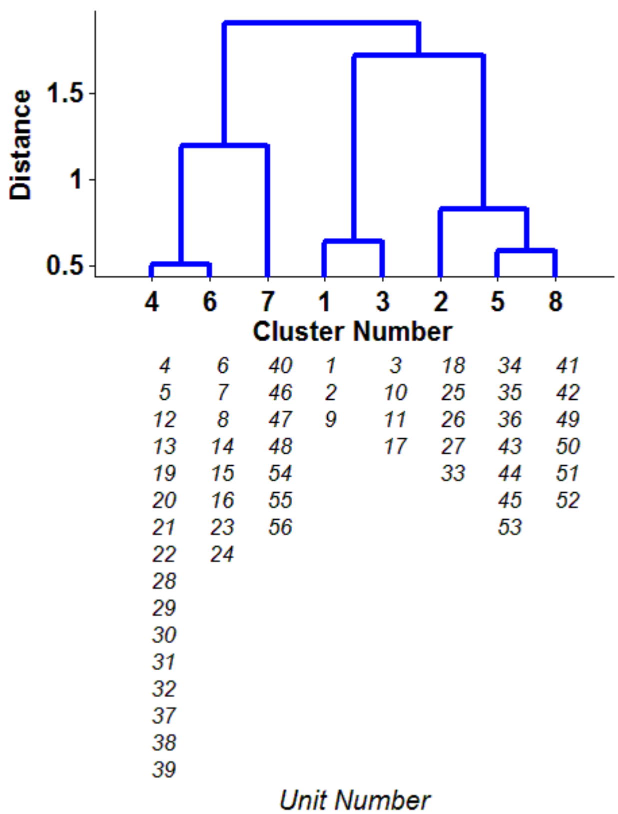

Fig. 4-3 Dendrogram with node numbers classified into the respective clusters.

Fig. 4-4 shows the pattern classification map of the 8 clusters, in which the numbers in the nodes represent Well Nos; the characters D and R correspond to the dry and rainy seasons; and the last characters u, m, and d denote upstream, middle-stream, and downstream areas, respectively. Simultaneous analysis of **Fig. 4-1** (component SOM maps) and **Fig. 4-4** reveals what kind of data the respective clusters include. For example, Cluster 1 (upper left part of **Fig. 4-4**) is associated with high-salinity water characterized by high Na^{+}, K^{+}, Mg^{2+}, and Cl^{-}, which is observed in the same location of the respective component SOM maps as shown in **Fig. 4-1**. On the other hand, the groundwater samples in nodes with extremely low concentrations of all ions are located at the lower left part of each SOM map (classified as Cluster 6), as shown in **Fig. 4-1**.

4.3.2 Fundamental characteristics of the respective clusters

The reference vector values of each node obtained from the SOM can provide quantitative information. In order to numerically characterize the classified data, the first quartile, median, and third quartile of the reference vector values for the 8 clusters were calculated. **Fig. 4-5** displays the radar charts of the 8 parameters for the 8 clusters with the first quartile, median, and third quartile plotted. As shown in this figure, the visible patterns of Clusters 1 and 3 are similar (as mentioned above for **Fig. 4-3**). Both the clusters have the pattern of significantly high values of all cations and Cl^{-} and very low values of HCO_3^{-} and CO_3^{2-}. In particular, Cluster 1 with the highest Na^{+} and Cl^{-} values represents the most saline water type of all the clusters. Clusters 4 and 6 have low concentrations of all the major ions, and it can be assumed that the wells in these clusters are of freshwater type. In particular, Cluster 6 with the lowest concentrations of all ions represents the freshest water type. Clusters 5 and 8 have similar ion patterns with significantly high values of Ca^{2+} and HCO_3^{-}, in which Cluster 8 has higher concentrations of all major ions than Cluster 5. Cluster 2 is characterized by high Ca^{2+}, SO_4^{2-}, Mg^{2+}, and HCO_3^{-} and low Na^{+}, Cl^{-}, K^{+}, and CO_3^{2-}, which according to **Fig. 4-3**, is close to the water type of Clusters 5 and 8. Cluster 7 shows a pattern where almost all ions have low values except CO_3^{2-} and HCO_3^{-}, which is close to the freshwater type (Clusters 4 and 6).

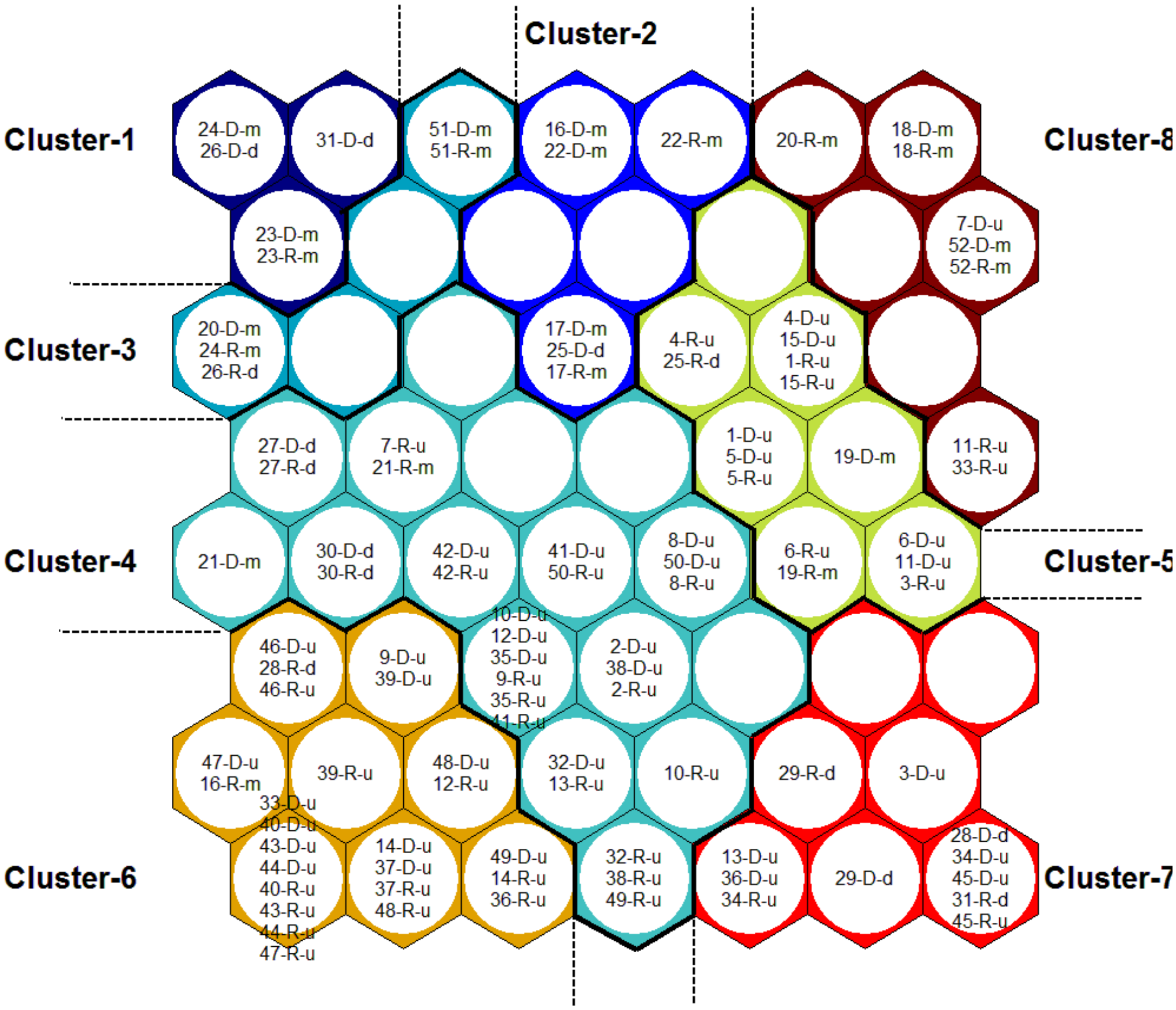

Fig. 4-4 Pattern classification map of the eight clusters by the SOM.

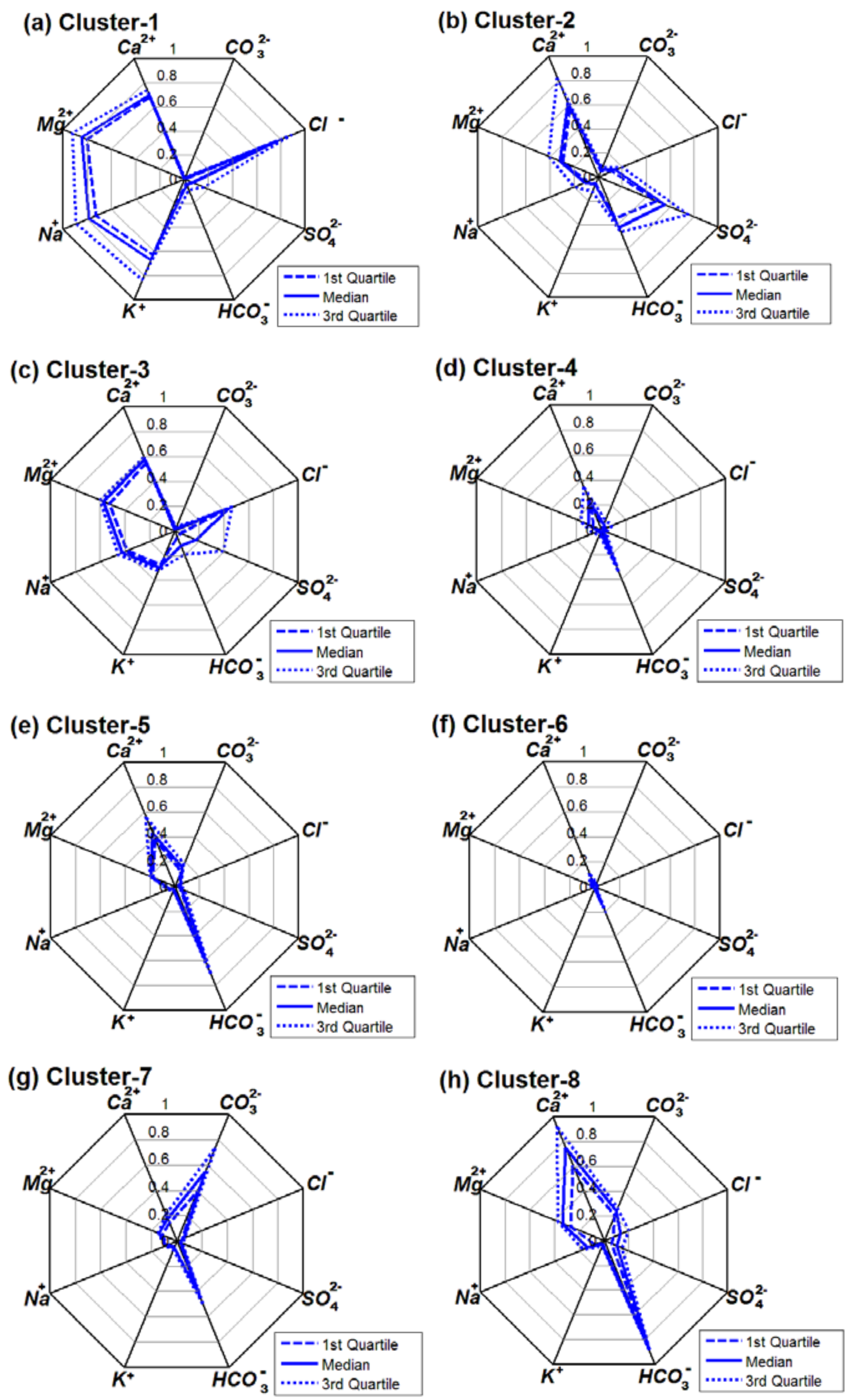

Fig. 4-5 Radar charts for the respective clusters with the first quartile (dashed lines), median (solid lines) and the third quartile (dotted lines) by obtained reference vectors.

To summarize, the 8 classified clusters could be divided into three main water types. The freshwater type was associated with Clusters 4, 6, and 7 due to the low values of Na^+ and $Cl^–$, as indicated in the lower part of **Fig. 4-5**. Clusters 1 and 3 were characterized by high concentrations of all cations and $Cl^–$ ion, representing the high-salinity type, as seen in the upper left part of **Fig. 4-5**. The remaining 3 clusters (Clusters 2, 5, and 8) were characteristic of the low-salinity type, as shown in the upper right part of **Fig. 4-5**.

Table 4-2 shows the mean, maximum, and minimum values calculated from the observed 8 parameters for each cluster and the whole data. Clusters 1 and 3 show considerably higher mean values of cations and $Cl^–$ than those for the whole data, indicating the most saline groundwater in the study area. In contrast, Clusters 4, 6, and 7 indicate lower mean values of almost all ions, particularly Cluster 6 with the lowest values confirming that the clusters represent the freshwater type, as mentioned above. Cluster 8 shows relatively higher values of almost all ions except K^+ than those for the whole data, while Cluster 5 shows slightly lower values. Cluster 2 indicates the highest $SO_4^{2–}$ mean value and slightly higher mean values of Ca^{2+}, Mg^{2+}, $HCO_3^–$, and $Cl^–$ than those for the whole data.

4.3.3 Seasonal changes in the respective clusters

Fig. 4-6 displays the SOM map, in which all the observation wells showing cluster changes from the dry to rainy seasons are indicated. From this figure, it is observed that 16 out of the 52 observation wells exhibited seasonal changes, in which 6 wells (Well Nos. 3, 7, 16, 20, 31, and 33) showed changes of water types and the other 10 wells showed changes within the same water type.

With regard to changes in water types, it is noted that samples from Well No. 31 changed from the high-salinity type (Cluster 1) to the freshwater type (Cluster 7). In fact, Well No. 31 is located in the southern coastal area, as shown in **Fig. 2-3**. According to Wagner et al. (2012), in this region there is a constant influx of fresh groundwater from the adjacent mountain coming to the aquifer. The increase of the groundwater recharge during

Table 4-2 Statistical descriptions of each cluster and the whole data

Cluster	Statistical value	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	CO_3^{2-} (mg/L)
Cluster 1	Mean	113.57	146.19	1387.54	81.20	86.58	10.81	2860.21	0.00267
	Min	75.15	105.55	600.00	40.50	15.26	0.00	1795.99	0.00003
	Max	175.55	249.28	3300.00	197.50	208.14	48.03	6292.38	0.01009
Cluster 2	Mean	93.02	51.17	138.71	7.58	266.71	157.77	338.84	0.00555
	Min	74.15	33.44	7.25	2.25	146.45	12.01	186.11	0.00360
	Max	110.22	71.13	195.00	12.50	315.78	456.29	475.03	0.00749
Cluster 3	Mean	87.35	85.26	474.99	13.22	91.56	34.17	1111.71	0.00315
	Min	62.63	72.05	306.45	8.01	15.40	0.00	907.52	0.00024
	Max	118.24	97.06	651.52	25.80	201.37	96.06	1490.67	0.00566
Cluster 4	Mean	41.50	20.01	51.86	3.89	203.35	6.78	99.51	0.00760
	Min	7.29	7.29	5.25	1.05	18.31	0.00	1.08	0.00006
	Max	73.15	45.60	188.00	10.10	360.02	31.22	464.40	0.02203
Cluster 5	Mean	72.18	28.45	73.37	4.13	414.33	10.40	114.96	0.01798
	Min	41.08	13.38	8.60	1.10	308.15	0.00	7.09	0.00261
	Max	103.21	54.72	340.00	8.90	500.36	36.02	538.84	0.04026
Cluster 6	Mean	18.21	8.83	29.08	2.80	117.77	3.87	45.52	0.00448
	Min	0.88	1.88	4.00	0.95	30.51	0.00	5.32	0.00005
	Max	35.57	17.18	90.00	6.35	198.32	19.21	180.80	0.02246
Cluster 7	Mean	31.23	23.53	137.85	7.94	272.65	8.15	192.61	0.07371
	Min	14.03	8.51	19.50	1.85	201.37	0.00	12.94	0.03082
	Max	85.17	47.18	365.00	20.80	421.04	20.38	623.92	0.14451
Cluster 8	Mean	113.67	66.63	254.66	5.73	599.52	20.08	533.53	0.02836
	Min	40.08	31.01	5.25	1.60	253.23	2.30	13.29	0.00615
	Max	205.40	110.96	725.00	7.85	835.97	78.05	1641.34	0.04994
Whole data	Mean	53.43	33.50	163.75	8.61	243.68	17.99	327.19	0.01637
	Min	0.88	1.88	4.00	0.95	15.26	0.00	1.08	0.00003
	Max	205.40	249.28	3300.00	197.50	835.97	456.29	6292.38	0.14451

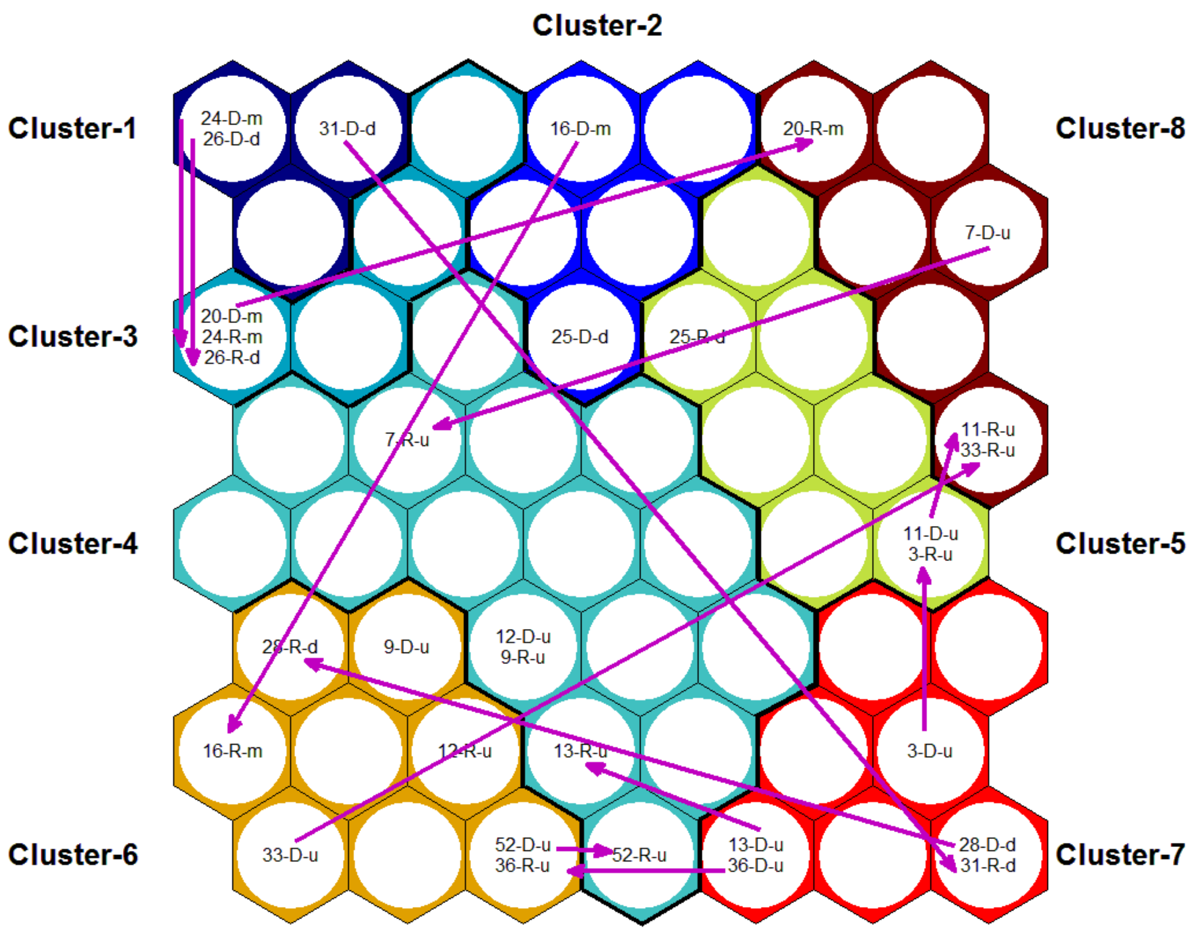

Fig. 4-6 Representation of the sampling points showing the changes in clusters from the dry to the rainy seasons.

the rainy season may be the reason causing the change in the water type of this well. Furthermore, samples from Well Nos. 16 and 7 changed from Clusters 2 and 8 (the low-salinity type) to Clusters 6 and 4 (the freshwater type), respectively, and Well No. 20 changed from Cluster 3 (the high-salinity type) to Cluster 8 (the low-salinity type). These changes imply that water infiltration from the HUA may affect the concentrations of chemical constituents of the PCA groundwater during the rainy season through hydrogeochemical windows, where the aquitard sandwiched by the aquifers is completely missing (Bui et al., 2012). Interestingly, samples from Well Nos. 3 and 33 located near the western boundary in the upstream area (as shown in **Fig. 2-3**) changed from Clusters 7 and 6 (the freshwater type) to Clusters 5 and 8 (the low-salinity type), respectively, which were characterized by high values of Ca^{2+} and HCO_3^-. According to Tran et al. (2012), the PCA in the RRD is recharged mainly from the surrounding mountains, in which the western mountains are carbonate rock formations consisting of marble, limestone, and dolomite (Drogue et al., 2000). This suggests that the increase of groundwater recharge from the western mountains during the rainy season, which causes the increase of dissolution of carbonate minerals, is the reason for these changes.

Regarding changes in clusters within the same water type, most observation wells exhibited the changes from the cluster with higher concentrations of most major ions in the dry season to the cluster with lower concentrations in the rainy season. For example, within the high-salinity type, samples from Well Nos. 24 and 26 changed from Cluster 1 to Cluster 3; within the freshwater type, Well No. 12 changed from Cluster 4 to Cluster 6; and within the low-salinity type, Well No. 25 changed from Cluster 2 to Cluster 5. The increase of groundwater recharge during the rainy season may create a dilution effect, which could explain the downward trends in the ion concentrations during the rainy season.

4.3.4 Spatial distribution of the respective clusters

Fig. 4-7 shows the spatial distribution of the 8 clusters classified by the SOM in the RRD. The symbols star, triangle, asterisk, circle, diamond, rectangular, cross, and inverse triangle represent Clusters 1–8, respectively. The white and black colors correspond to the

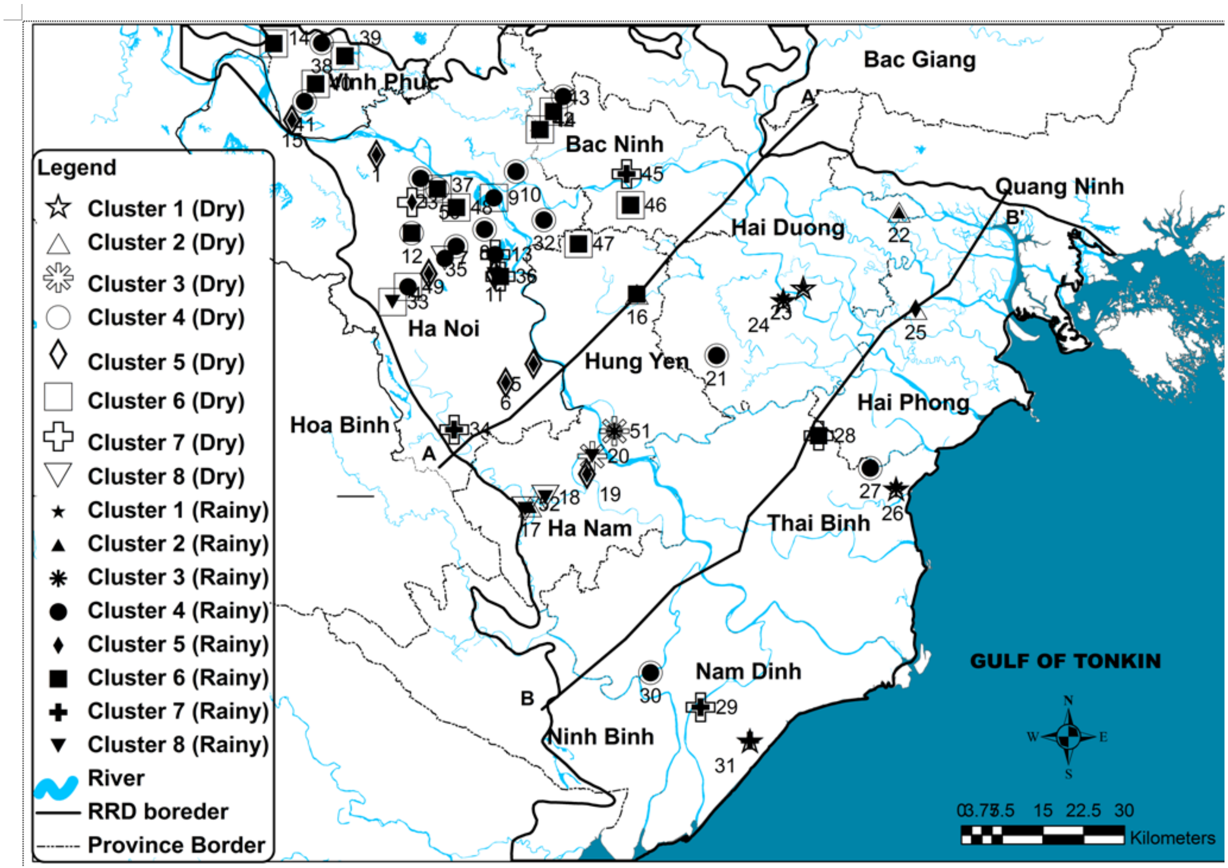

Fig. 4-7 Spatial distribution of the respective clusters.

dry and rainy seasons, respectively. As seen in this figure, observation well locations are unevenly distributed across the study area. Due to the region's importance, the wells are denser in urbanized areas, especially around Hanoi. Therefore, well density should be taken into consideration while discussing the spatial distribution of the clusters.

Besides the fact that Clusters 1 and 3 (the high-salinity type) are observed in the coastal area, such as Well Nos. 26 and 31, they are also found in the middle-stream area (Well Nos. 20, 23, 24, and 51), as shown in **Fig. 4-7**. Saltwater intrusion could be the reason for the presence of the high-salinity type in the coastal area. However, high salinity in the middle-stream area could be due to leaching of salty paleowater. According to Tanabe et al. (2003), during the Holocene, the sea transgressed the flood plain as far inland as the present location of Hanoi. The transgression during the Holocene, induced by sea-level rise, must have caused an intrusion of seawater into the underlying highly permeable Pleistocene sediment and the salty porewater may still be present in the middle-stream area.

It is noted that the low salinity type clusters (Clusters 2, 5, and 8) were found near the western and northeastern boundaries of the RRD. Clusters 5 and 8 characterized by high Ca^{2+} and HCO_3^- were distributed near the western boundary, while Cluster 2 with significantly high Ca^{2+} and SO_4^{2-} is found near the northeastern boundary. Ca^{2+} and HCO_3^- are released by the dissolution of carbonate rock (Jalali, 2009). In fact, the mountains near the western boundary of the delta, which are the main recharge zones for the PCA, are carbonate rock formations comprising marble, limestone, and dolomite (Drogue at al., 2000). This suggests that dissolution of these minerals will add significant amounts of Ca^{2+} and HCO_3^- to the groundwater near the western boundary of the RRD. On the other hand, high Ca^{2+} and SO_4^{2-} (Cluster 2) probably resulted from the dissolution of sulfate minerals (gypsum and anhydrite), which are commonly found in the Quaternary aquifer system (El-Fiky, 2009). The freshwater type clusters (Clusters 4, 6, and 7) were distributed mostly in the upstream and downstream areas except the coastal area, in which the freshest water type cluster (Cluster 6) was found in the upstream area, as shown in **Fig. 4-7**.

4.3.5 Factors governing water chemistry

Fig. 4-8 shows the Gibbs diagram for the 8 clusters classified by the SOM. The symbols for expressing the Clusters 1–8 in this figure are the same as that in **Fig. 4-7**. Gibbs (1970) found that most of the world’s surface water falls within the boomerang-shaped boundaries. Based on analytical chemical data for numerous surface samples, Gibbs theorized the three major mechanisms controlling world surface water chemistry, which are presented in three domains: precipitation dominance (lower part), rock dominance (middle part), and evaporation dominance (upper part), as shown in **Fig. 4-8**. In addition, as mentioned in the introduction, Gibbs diagram has been also used for the functional sources assessment of dissolved ions in groundwater in various studies (Raju et al., 2011; Marghade et al., 2012; Yidana et al., 2010). Clusters 1 and 3 (the high-salinity type) were plotted

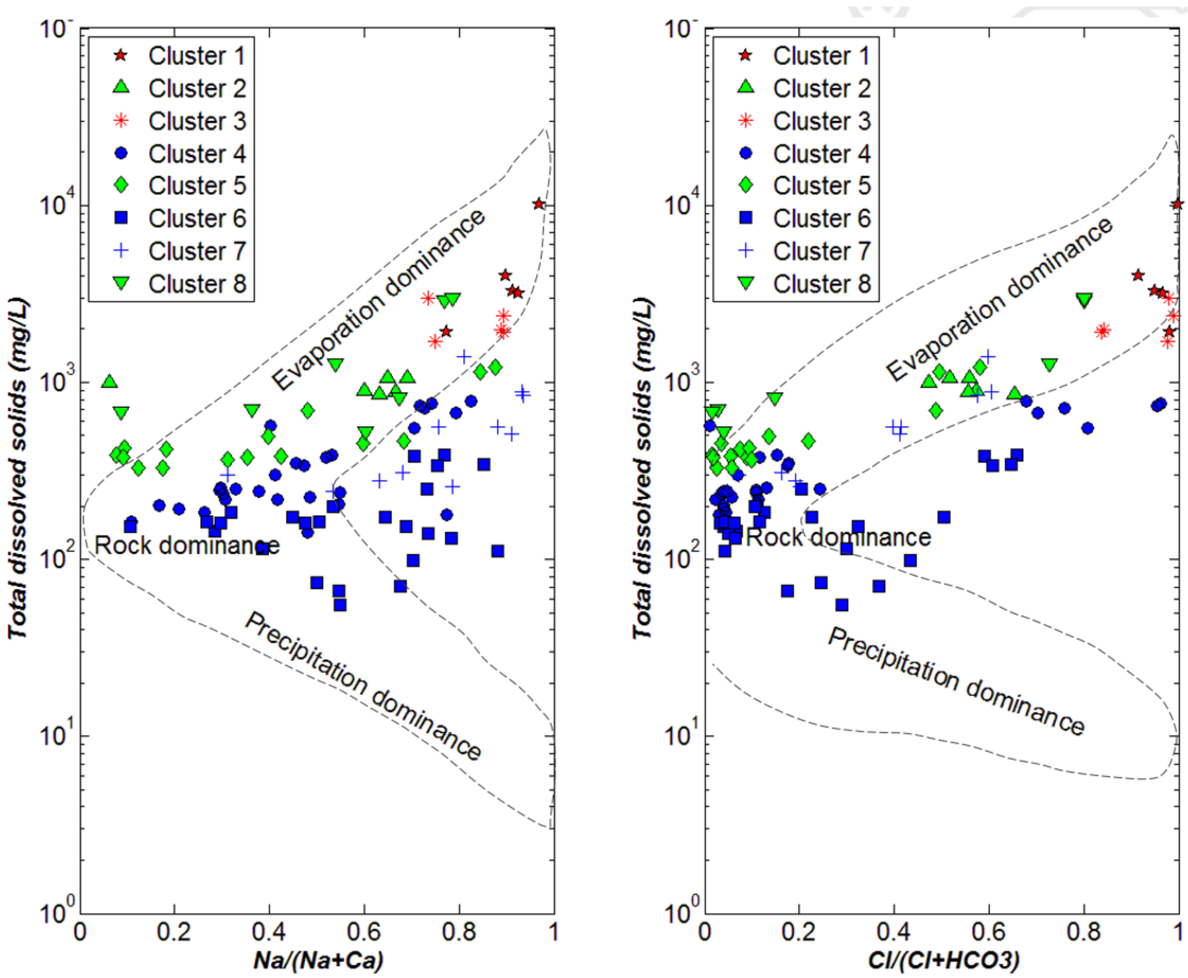

Fig. 4-8 Gibbs diagrams for the classified groundwater data into the respective cluster.

toward the evaporation dominance domain as the result of high TDS and weight ratios (Na/Ca+Na and Cl/Cl+HCO_3). The high TDS is due to high concentrations of Na^+ and $Cl^−$ (as shown in **Table 4-2**). This suggests that marine activities, such as saltwater intrusion and salty paleowater, are the main factor affecting the groundwater chemistry of these clusters.

On the other hand, groundwater samples belonging to Clusters 4, 6, and 7 (the freshwater type) fall toward the domain of rock dominance due to low TDS. Some samples belonging to these clusters fall outside the boomerang-shaped boundaries. It is common for groundwater that the domain of rock dominance extends further toward higher weight ratios (Raju et al., 2011; Marghade et al., 2012; Yidana et al., 2010). The fall in the rock dominance domain suggests that these clusters are dominated by the processes of mineral dissolution. In particular, Cluster 6 has the lowest TDS with some samples tending to fall in the domain of precipitation dominance. This explains why this cluster has the lowest concentrations of all ions (**Table 4-2**).

In the low-salinity type, Clusters 2 and 8 have relatively high TDS as a result of the high concentrations of Ca^{2+} and $SO_4^{2−}$ for Cluster 2 and Ca^{2+} and $HCO_3^−$ for Cluster 8, and thus, falling in the evaporation dominance domain. This could be due to evaporation, which increases salinity and precipitation of $CaCO_3$ from solution, which increases the relative proportion of Na^+ to Ca^{2+} and $Cl^−$ to $HCO_3^−$ (Gibbs, 1970). Cluster 5 falls in the rock dominance domain, which suggests that rock–water interaction is the natural mechanism controlling the dissolved ions in this cluster.

4.4 Results and discussion for HUA

4.4.1 SOM and clustering results

The input data for the SOM application were varying concentrations of eight chemical parameters (major ions Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, Cl^- and CO_3^{2-}) from 94 samples, which were observed in 47 HUA wells during the dry and rainy seasons. Based on the methodology described above, the number of SOM nodes was calculated as 44, and the numbers of rows and columns were 11 and 4, respectively. The constructed SOM was used for the cluster analysis of the standardized groundwater chemistry monitoring data.

Fig. 4-9 shows the eight-component SOM maps finally obtained after the training process. Each map represents the component value of the reference vectors for the 44 SOM nodes, in which the reference vectors were standardized to range 0–1, using gradient of color. The nodes that represent high values are red and those representing low values are blue. A comparison by means of a gradient of colors among the component SOM maps can indicate informative and qualitative relations (or correlations) among the studied parameters. Through visual investigation of the SOM maps shown in **Fig. 4-9,** Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, and SO_4^{2-} have similar gray gradients. This means that there is strong positive correlation among these five parameters. Similarly, CO_3^{2-} showed a positive correlation with HCO_3^{-}, while the component SOM map of Ca^{2+} did not show any correlation with the other parameters.

Table 4-3 shows the correlation coefficients among eight physicochemical parameters using the standardized reference vectors. This table quantitatively confirms the strength of the relations between these parameters. For example, the relation of Cl^{-} with Mg^{2+}, K^{+}, Na^{+}, and SO_4^{2-} indicated significantly high correlation coefficients more than 0.88. CO_3^{2-} also showed a strong correlation with HCO_3^{-} with the correlation coefficient of 0.95, while the correlation coefficients of Ca^{2+} with other parameters were relatively low, as shown in **Table 4-3**.

In order to select the optimal number of clusters, the DBI values based on the k-means clustering algorithm were calculated for the minimum (2) to the maximum (44) possible clusters. **Fig. 4-10** shows the variation of the DBI values after being applied to the data. The most appropriate number of clusters corresponding to the minimum DBI was five. Once the optimum number of clusters had been selected, the hierarchical clustering algorithm using Ward's method was applied to obtain the five clusters for fine-tuning the pattern classification.

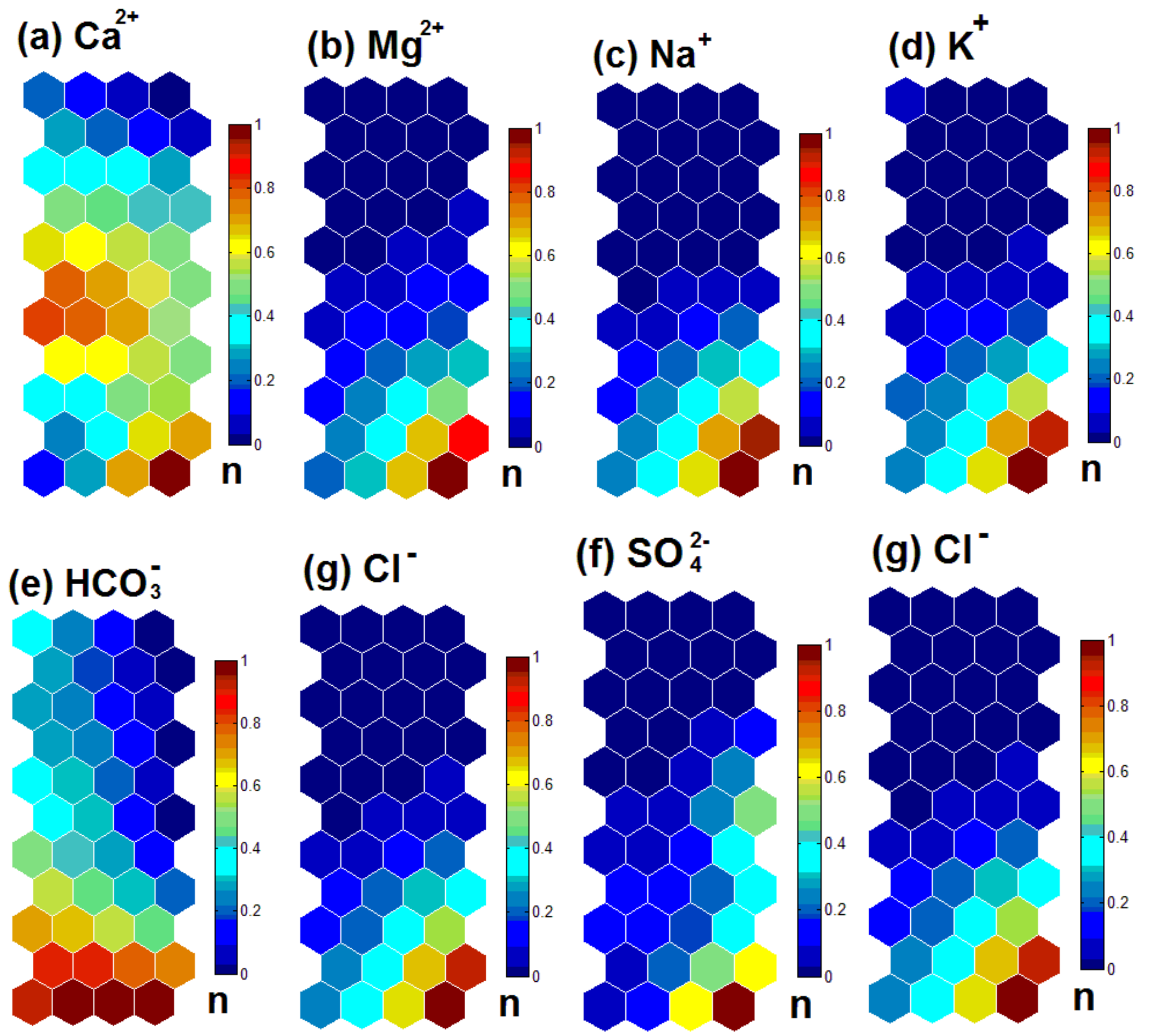

Fig. 4-9 Component planes for (a) Ca^{2+}, (b) Mg^{2+}, (c) Na^{+}, (d) K^{+}, (e) HCO_3^{-}, (f) SO_4^{2-}, (g) Cl^{-}, (i) CO_3^{2-}.

Table 4-3 Correlation coefficients among 8 physicochemical parameters in HUA

	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	$HCO3^{-}$	$SO4^{2-}$	Cl^{-}
Mg^{2+}	0.47						
K^{+}	0.44	0.996					
Na^{+}	0.43	0.996	0.998				
$HCO3^{-}$	0.30	0.72	0.74	0.71			
$SO4^{2-}$	0.54	0.89	0.86	0.87	0.46		
Cl^{-}	0.45	0.997	0.998	0.999	0.70	0.88	
$CO3^{2-}$	0.10	0.67	0.69	0.67	0.95	0.46	0.66

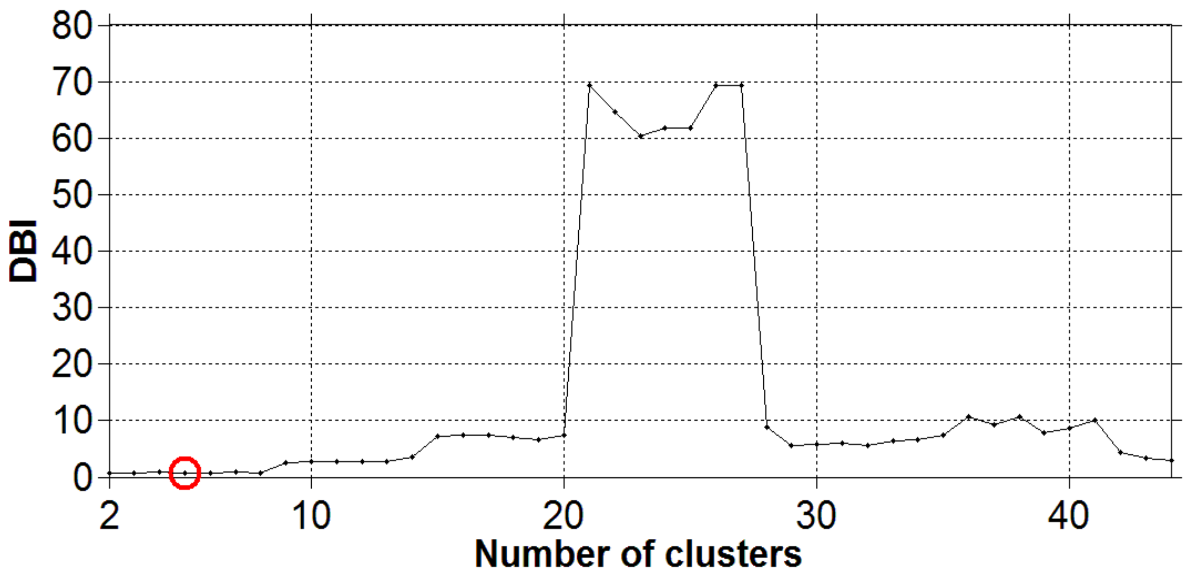

Fig. 4-10 Variation of DBI values with the optimal number of clusters marked by the circle on the figure.

Fig. 4-11 shows the hierarchical cluster tree with the nodes of the SOM classified into five different clusters. The nodes in the SOM map are numbered from top to bottom and from left to right. As shown in this figure, Clusters 1 and 5 have the smallest distance or highest similarity between clusters, implying that Clusters 1 and 5 have similar hydrogeochemical characteristics. In contrast, Cluster 4 and the other clusters are at relatively far distances, implying that the characteristics of Cluster 4 are different from the other clusters.

Fig. 4-12 shows the pattern classification map of the five clusters. The numbers represent Well Nos.; D and R denote the dry and rainy seasons; and u, m, and d denote upstream, middle-stream, and downstream areas, respectively. Simultaneous consideration of **Fig. 4-9** (the component SOM maps) and **Fig. 4-12** indicates the type of data included in the respective clusters. For example, Cluster 4 (lower right part of **Fig. 4-12**) is associated

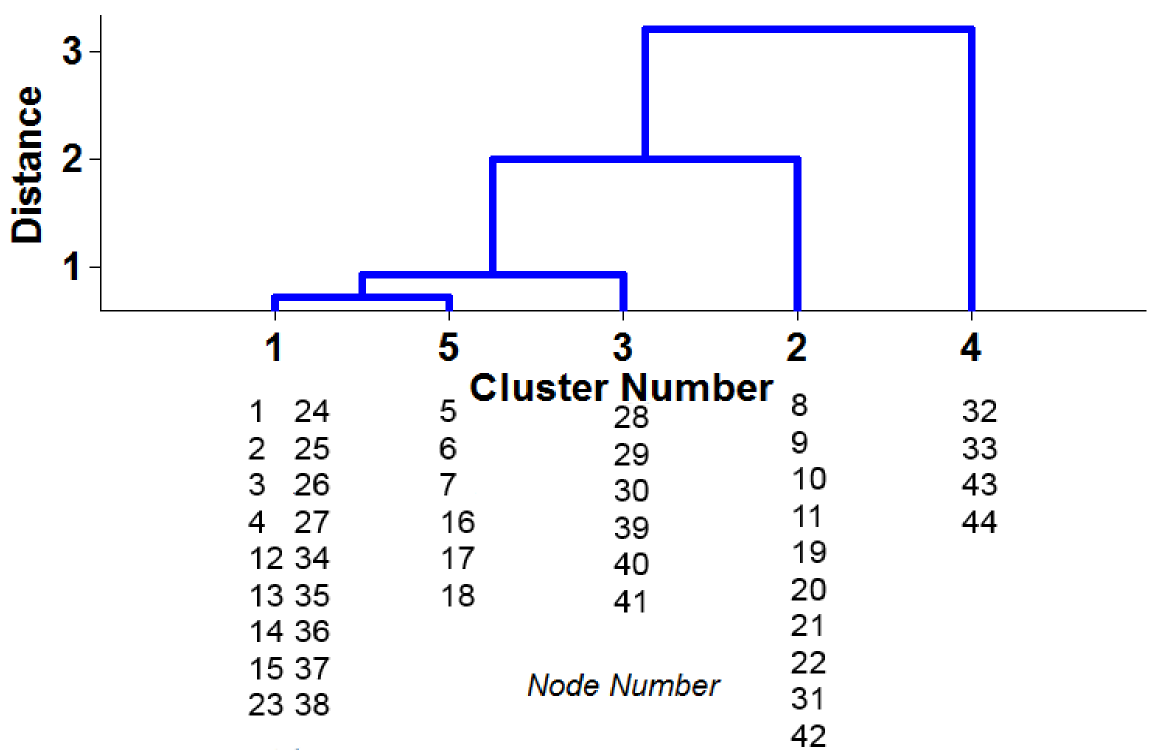

Fig. 4-11 Dendrogram with node numbers classified into the respective clusters.

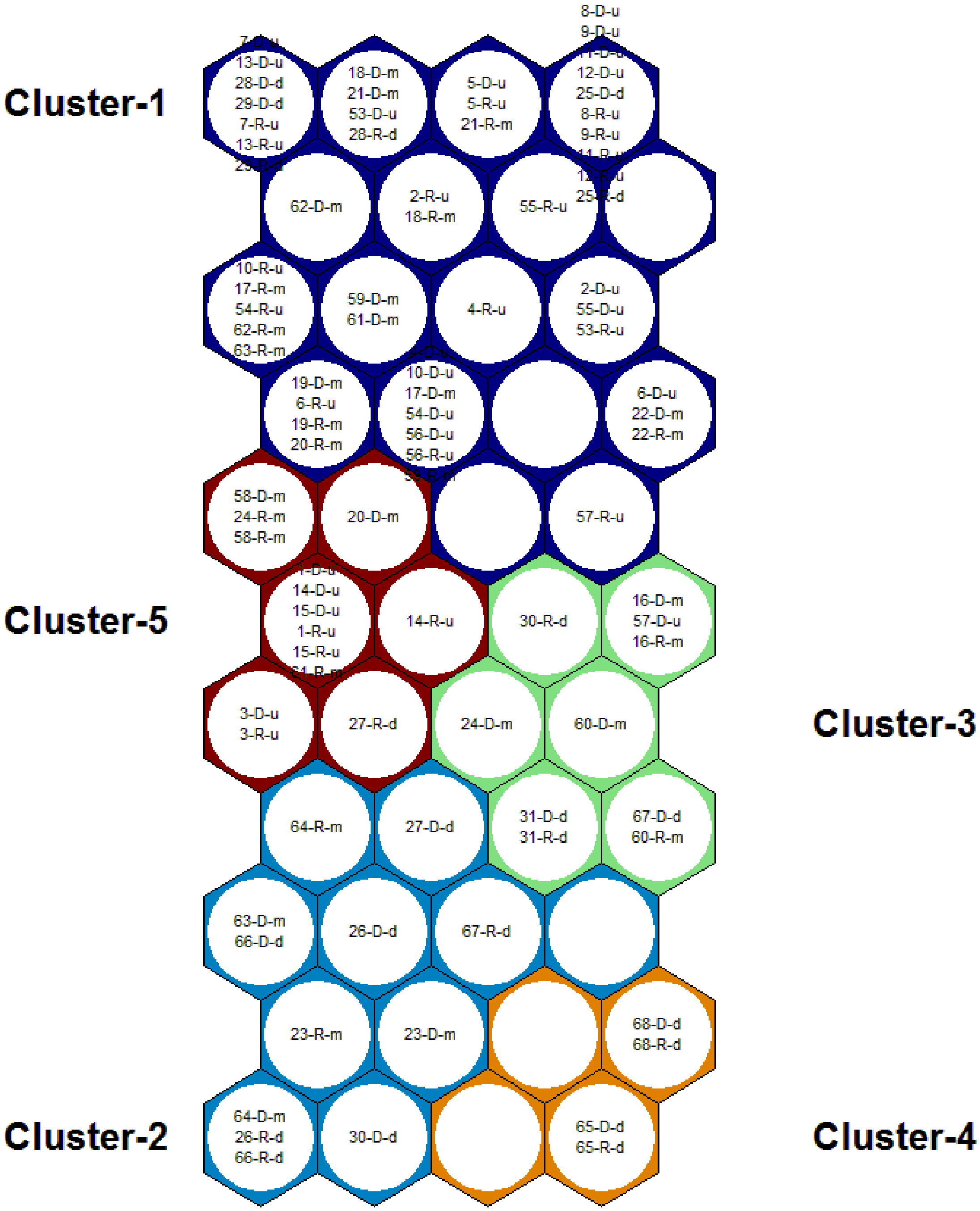

Fig. 4-12 Pattern classification map of the eight clusters by the SOM for HUA.

with high-salinity water characterized by significantly high concentrations of all ions, which is observed in the same location of the respective component SOM maps, as shown in **Fig. 4-9**. On the other hand, the groundwater samples in nodes with extremely low concentrations of almost all ions are located at the upper part of each SOM map (classified as Cluster 1), as shown in **Fig. 4-9**.

4.4.2 Fundamental characteristics of the respective clusters

The reference vector values obtained from the SOM can provide quantitative information. In order to numerically characterize the classified data, the first quartile, median, and third quartile for the five clusters were calculated using the reference vectors. **Fig. 4-13** displays the radar charts of the eight parameters for the five clusters with the first quartile, median, and third quartile plotted. As shown in this figure, the visible patterns of Clusters 1 and 5 are similar (as mentioned above for **Fig. 4-11**). Both clusters reveal a pattern of low concentration of all the major ions. In particular, Cluster 1, with the lowest values for all major ions, represents the freshest water type. The highest values of all ions are classified into Cluster 4; therefore, the samples in this cluster can be assumed to be of the high-salinity type. Clusters 2 and 3 include relatively high values for all cations and Cl^-. Furthermore, Cluster 2 is associated with much higher anions of CO_3^{2-} and HCO_3^-. In this study, both Clusters 2 and 3 were classified as the low-salinity type, even though the distance between the clusters is quite far, as can be seen in **Fig. 4-11**.

To summarize, the five classified clusters could be divided into three main water types on the basis of the values of all major ions. The freshwater type was associated with Clusters 1 and 3 due to the lowest values for all ions, as indicated in the upper and middle-left parts of **Fig. 4-12**. Cluster 4 was characterized by high concentrations of all major ions, representing the high-salinity type, as seen in the lower right of **Fig. 4-12**. The remaining two clusters (Clusters 2 and 3) are characteristic of the low-salinity type, as shown in the lower-left and middle-right parts of **Fig. 4-12**.

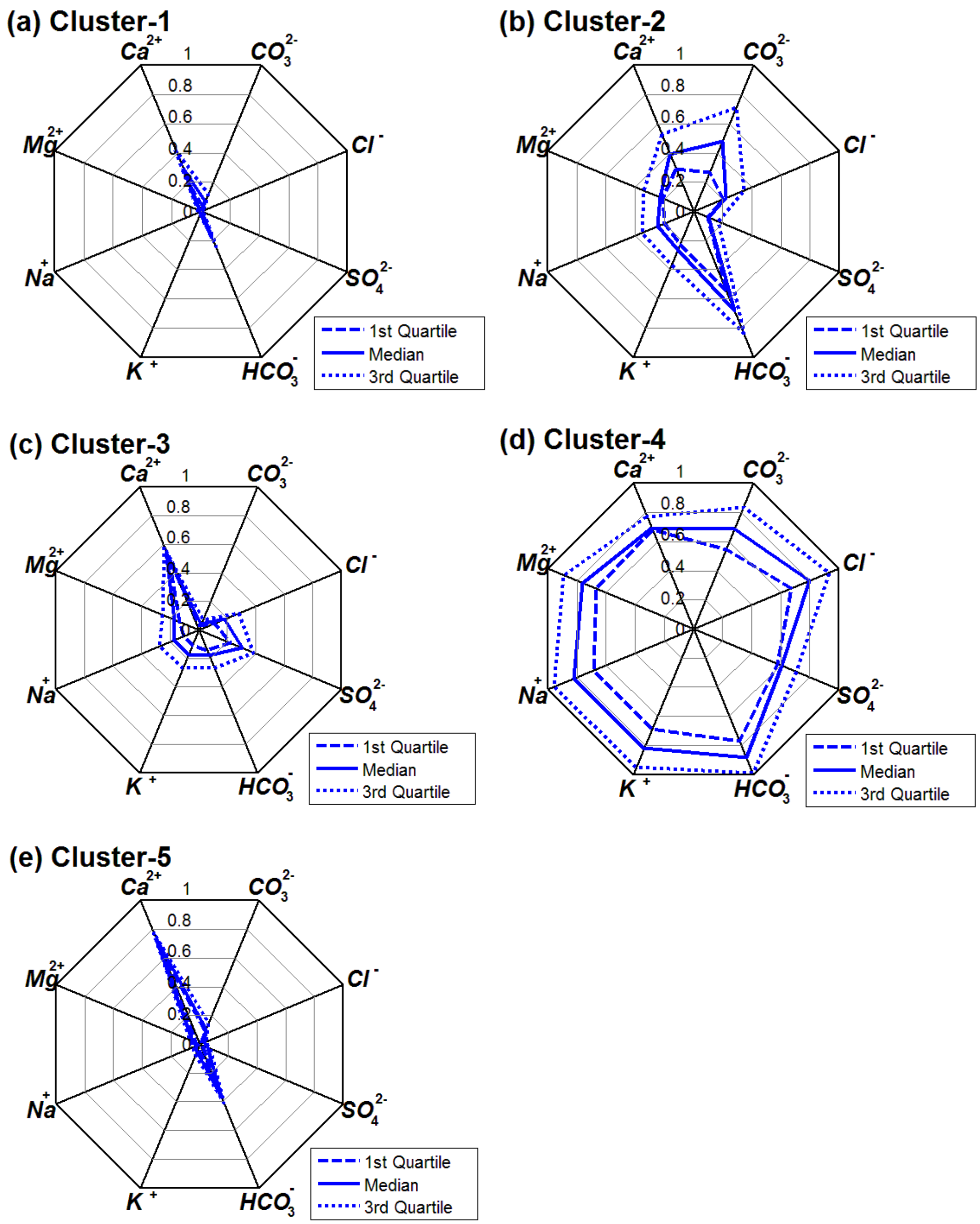

Fig. 4-13 Radar charts for the respective clusters with the first quartile (dashed lines), median (solid lines) and the third quartile (dotted lines) by obtained reference vectors.

Table 4-2 shows the mean values calculated from the observed eight parameters for each cluster and the whole data. Clusters 1 and 5 indicate lower mean values for almost all ions. Particularly Cluster 1 had the lowest values, except for CO_3^{2-}. These values confirm that Clusters 1 and 5 represent the freshwater type, as mentioned above. In contrast, Cluster 4 shows considerably higher mean values than those for the whole data for all major ions, indicating the most saline groundwater in the study area. Clusters 2 and 3 have relatively higher mean values for almost all ions compared to the values for the whole data.

4.4.3 Seasonal changes in the respective clusters

Fig. 4-14 displays the SOM map, in which all the observation wells showing cluster changes from the dry to rainy seasons are indicated. From this figure, eight out of the 47 observation wells were observed to exhibit seasonal changes. Four wells (Well Nos. 24, 27, 57, and 63) showed changes of water types and the other four wells (Well Nos. 20, 30, 61, and 67) showed changes within the same water type.

Samples from each of the four wells that exhibited changes in water type changed from the low-salinity to the freshwater type. In other words, observation wells exhibited changes from the cluster with higher concentrations of most ions in the dry season to the cluster with lower concentrations in the rainy season. The increase of groundwater recharge, e.g., from rainfall and rivers, may create a dilution effect, which could explain the downward trends in the ion concentrations during the rainy season.

In terms of changes in clusters within the same water type, samples from Well No. 30 notably changed from Cluster 3 (the low-salinity type with relatively high SO_4^{2-} and low CO_3^{2-} and HCO_3^-) to Cluster 2 (the low-salinity type with high CO_3^{2-} and HCO_3^-), while Well No. 67 changed from Cluster 2 to Cluster 3. As shown **in Fig. 2-3**, Well No. 30 is located in the southwest downstream area, whereas Well No. 67 is situated in the northeast downstream area. According to Bui et al. (2012), the HUA in the RRD is recharged primarily from rivers and the surrounding mountains. The western mountains are carbonate rock formations consisting of marble, limestone, and dolomite, whereas sulfate minerals

Table 4-4 Mean values of eight parameters for the five clusters and whole data

Cluster	Statistical value	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	CO_3^{2-} (mg/L)
Cluster 1	Median	70.13	31.29	77.90	5.62	366.32	23.46	134.84	0.02590
	Min	20.79	4.59	3.50	0.40	57.97	0.00	6.20	0.00040
	Max	118.24	123.42	746.00	34.50	753.60	386.64	1159.22	0.11205
Cluster 2	Median	69.93	172.40	1327.08	58.23	911.74	85.35	2185.35	0.13811
	Min	15.03	82.08	450.00	18.20	591.89	0.00	629.24	0.02350
	Max	145.29	322.24	2240.00	81.00	1238.71	300.19	3864.05	0.26910
Cluster 3	Median	105.41	154.47	1306.15	45.80	301.13	352.45	2313.29	0.01041
	Min	37.58	69.31	30.50	5.35	70.17	0.00	30.13	0.00009
	Max	190.38	291.84	2800.00	89.00	546.13	946.19	4741.44	0.03252
Cluster 4	Median	155.89	779.00	6800.00	256.00	1051.03	771.48	11618.32	0.17895
	Min	57.62	644.48	6300.00	229.00	715.00	0.00	8603.80	0.02818
	Max	280.56	1076.16	7200.00	272.50	1372.95	1753.10	13391.24	0.40359
Cluster 5	Median	138.17	51.61	107.60	11.36	586.58	48.53	191.62	0.03093
	Min	104.21	16.41	14.00	0.85	414.94	0.00	14.18	0.00873
	Max	175.35	224.96	605.00	40.50	808.52	308.21	1267.34	0.09355
Whole data	Median	87.64	97.25	658.51	28.12	490.95	101.93	1125.47	0.04584
	Min	15.03	4.59	3.50	0.40	57.97	0.00	6.20	0.00009
	Max	280.56	1076.16	7200.00	272.50	1372.95	1753.10	13391.24	0.40359

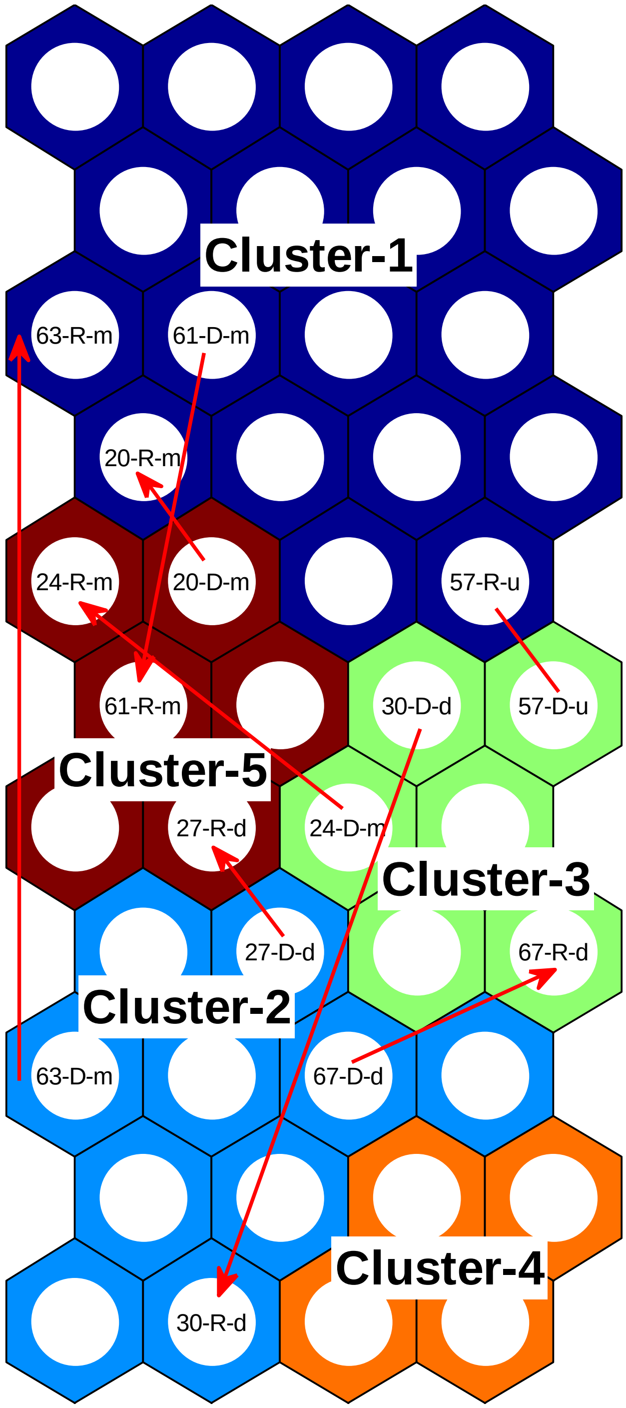

Fig. 4-14 Representation of the sampling points showing the changes in clusters from the dry to the rainy seasons.

(gypsum and anhydrite) are commonly found in the northeast mountain area (Drogue et al., 2000). This suggests that the increase of groundwater recharge from the mountains during the rainy season, which causes increased dissolution of carbonate minerals in Well No. 30 and sulfate minerals in Well No. 67, could be the reason for these changes. On the other hand, samples from Well Nos. 20 and 61 changed from Cluster 5 to Cluster 1 (the lowest salinity). This may be due to the increase of groundwater recharge by surface water, such as rainfall, lakes or rivers, during the rainy season.

4.4.4 Spatial distribution of the respective clusters

Fig. 4-15 shows the spatial distribution of the five clusters classified by the SOM in the RRD. The symbols circle, triangle, cross star, and square represent Clusters 1–5, respectively. The white and black colors correspond to the dry and rainy seasons, respectively. As seen in **Fig. 4-15**, Cluster 4 (the high-salinity type) is observed in the coastal area, e.g., Well Nos. 65 and 68. Saltwater intrusion could be the reason for the presence of the high-salinity type in the coastal area.

Besides the fact that Clusters 2 and 3, characterized by the low-salinity type, are observed in the downstream area (Well Nos. 26, 27, 30, and 66), they are also found in the northeast part of the upstream and middle-stream areas (Well Nos. 16, 23, 24, 57, 60, and 63). Along the Red River and its tributaries, salty bottom water is transported as far inland as 35 km from the sea (Vu, 1996). This salty bottom water may leak into adjacent aquifers, either as a density-driven flow or as a downward flow controlled by a hydraulic gradient, where the river bottom sediments are highly permeable. Therefore, the low-salinity type found in the downstream is probably due to saltwater intrusion from the river. On the other hand, upon the closer inspection of land use, Well Nos. 16, 23, 24, 57, 60, and 63 (northeast part of the upstream and middle-stream areas) are located in an intensely irrigated agricultural area (Asian Development Bank, 2000). Thus, it is reasonable to infer that the presence of the low-salinity type in the upstream and middle-stream areas could be influenced by agricultural activities.

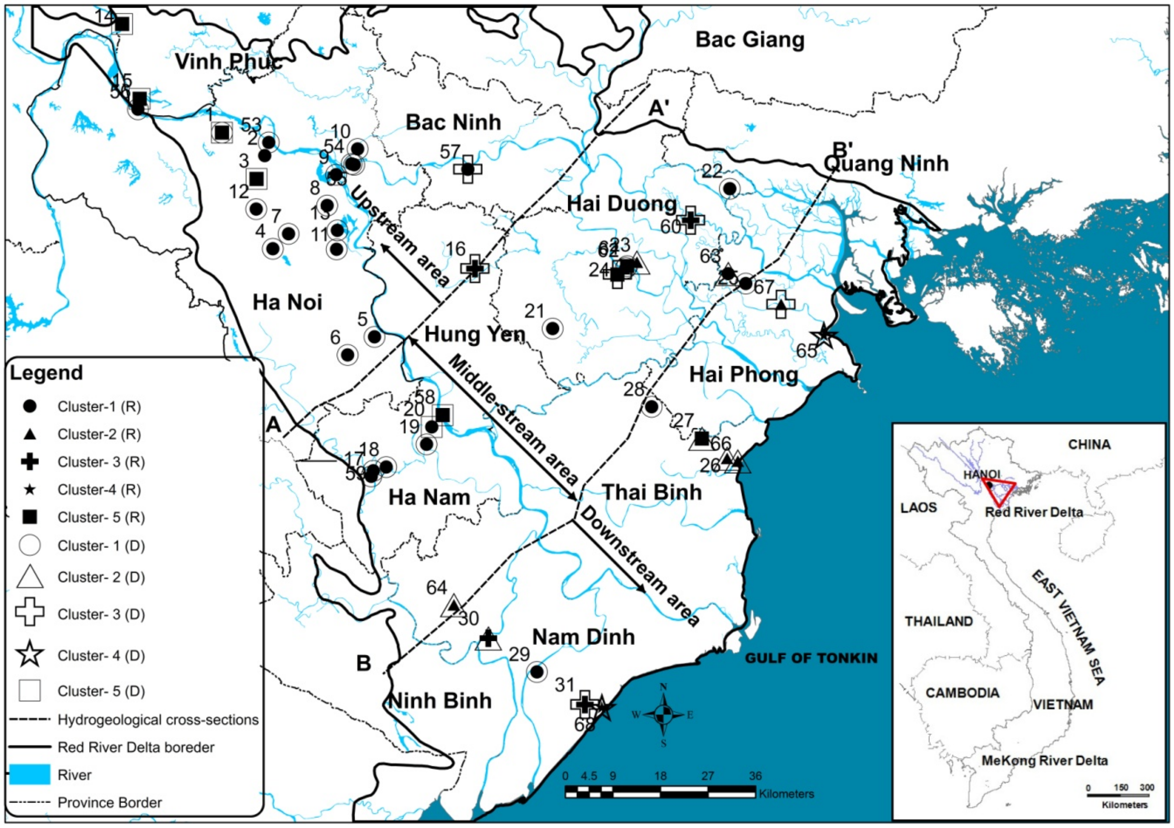

Fig. 4-15 Spatial distribution of the respective clusters.

Clusters 1 and 5, representing the freshwater type, are found not only in the upstream and middle-stream areas but also in the downstream area, as seen in Well Nos. 27, 28 (northeast of the downstream area) and 29 (south of the downstream area). The presence of the freshwater type in the northeast of the downstream area implies that saltwater intrusion does not affect groundwater this far inland. On the other hand, Wagner et al. (2012) identified a local lens of freshwater existing in the south portion of the downstream area, which explains the presence of the freshwater type found in Well No. 29.

The samples showing cluster changes from the dry to the rainy seasons were primarily located in the middle-stream and downstream areas of the delta. This suggests that surface water strongly influences the chemical characteristics of unconfined groundwater at the middle-stream and downstream areas of the delta, but weakly influences the upstream area during the rainy season.

4.4.5 Factors governing water chemistry

Fig. 4-16 shows the Gibbs diagram for the five clusters classified by the SOM. The symbols representing Clusters 1–5 in this figure are the same as those in **Fig. 4-15**. Gibbs (1970) found that most of the world's surface water falls within the boomerang-shaped boundaries. Based on analytical chemical data for numerous surface samples, Gibbs theorized that three major mechanisms control world surface water chemistry. These mechanisms can be classified into three domains: precipitation dominance (lower part), rock dominance (middle part), and evaporation dominance (upper part), as shown in **Fig. 4-16**. Clusters 1 and 5 (the freshwater type) were plotted toward the rock dominance domain due to low TDS. Some samples in these clusters fell toward the evaporation dominance domain but no sample fell in the precipitation dominance domain. This suggests that Clusters 1 and 5 are dominated by rock mineral dissolution processes.

On the other hand, Cluster 4 (the high-salinity type) was plotted in the evaporation dominance domain with the highest TDS and significantly high ratios of Na/(Ca+Na) and Cl/(Cl+HCO_3). The high TDS is due to high concentrations of all ions (as shown in **Table 4-4**). This suggests saltwater intrusion is the main factor affecting the groundwater chemistry of this cluster. Furthermore, Clusters 2 and 3 (the low-salinity type) had relatively high TDS and high ratios of Na/(Ca+Na) and Cl/(Cl+HCO_3), and thus, they fell in the evaporation dominance domain. Anthropogenic and marine activities, such as intensive and long-term irrigation, agricultural fertilizers, and saltwater intrusion, could be the primary factors causing these clusters to fall into the evaporation dominant domain.

4.5 Conclusion

In this study, hydrogeochemical groundwater data comprising major ions from 52 PCA wells and 47 HUA wells that were obtained during the dry and rainy seasons in 2011 were classified using the SOM in combination with a hierarchical cluster analysis to

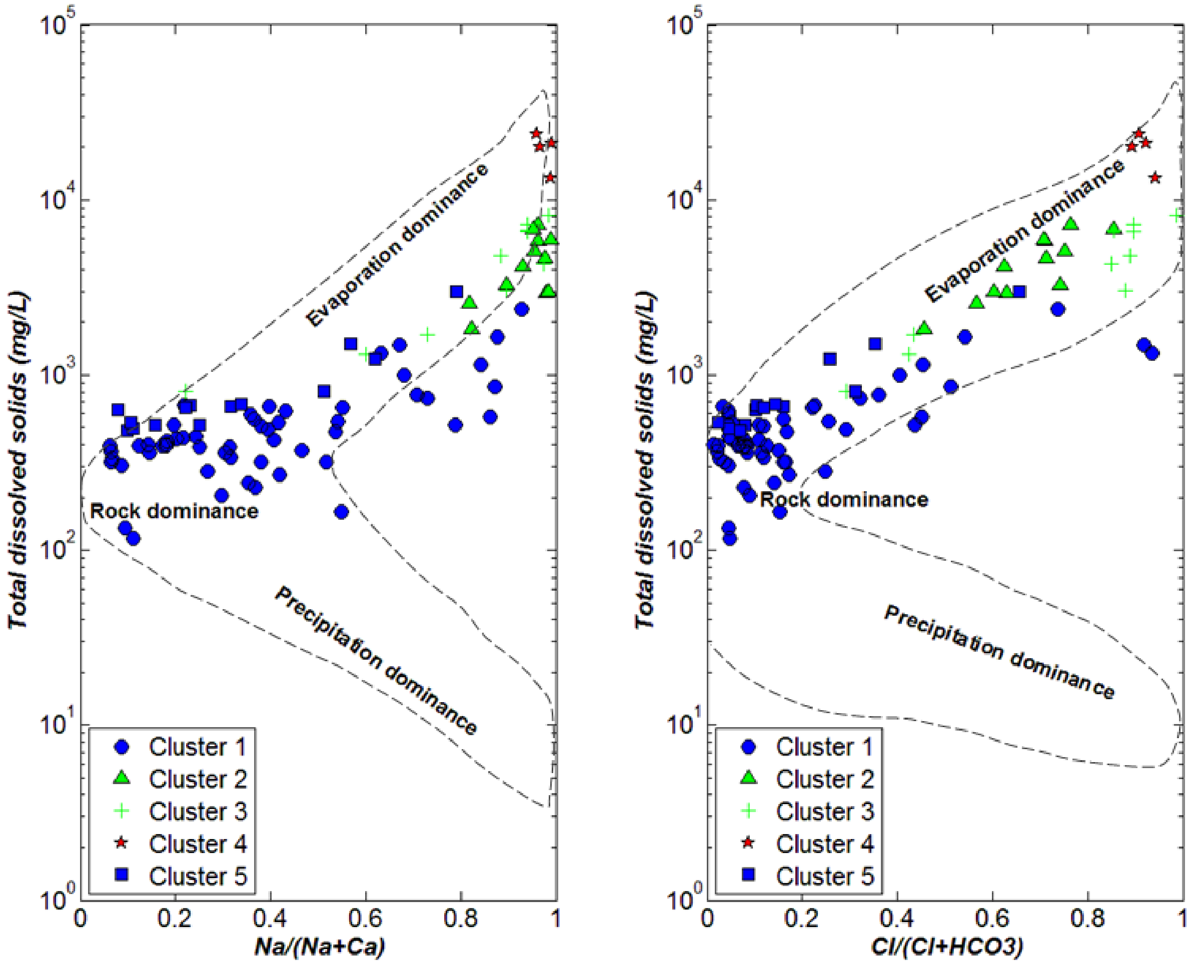

Fig. 4-16 Gibbs diagram for the classified groundwater data into the respective cluster.

investigate the seasonal and spatial hydrogeochemical characteristics of groundwater in the two main aquifers of the RRD. The SOM was systematically applied using a stepwise procedure, including transformation of data, establishment of the SOM structure, initialization of reference vectors, parameters training, selection of an optimal number of clusters, and a fine-tuning cluster analysis. The first, second, and third quartiles of the reference vectors were plotted on radar charts to display the fundamental characteristics of each cluster. In addition, Gibbs diagram was also created to elucidate the hydrogeochemical characteristics classified by the SOM. The main conclusions drawn from this study are as follows:

- From the results of the SOM application for PCA, the major ion chemistry data of PCA were divided into eight clusters, which revealed three basic representative water types characterized by the high salinity (Clusters 1 and 3), low salinity (Clusters 2, 5, and 8), and freshwater (Clusters 4, 6, and 7). The high-salinity water type is distributed in the middle-stream and coastal areas, while the low-salinity water type is found near the western and northeast boundaries of the RRD.
- The SOM application for HUA classified the major ion chemistry data of HUA into five clusters, which also revealed three basic representative water types characterized by the high salinity (Cluster 4), low salinity (Clusters 2 and 3), and freshwater (Clusters 1 and 5). The high-salinity type was located in the coastal area, whereas the low-salinity type samples were found not only in the downstream area but also in the northeastern parts of the upstream and middle-stream areas, where groundwater samples were mainly classified into Cluster 3. With closer inspection of land use, the groundwater of this cluster was considered to be contaminated by agricultural activities. The freshwater type was generally found in the upstream and middle-stream areas. However, some samples belonging to this type were also found in the northeastern and southern parts of the downstream area.
- For PCA, changes in the water types from the dry to rainy seasons were detected in more than 10% of the observation wells, while cluster changes within the same water type

was about 20%. The increase in groundwater recharge during the rainy season could be the main reason for these changes.

- For HUA, cluster changes from the dry to rainy seasons were detected in approximately one-fifth of the observation wells, mostly found in the middle-stream and downstream areas. This suggest strong influence of surface water on the chemical characteristics of unconfined groundwater at the middle-stream and downstream areas of the delta during the rainy season.

- The results of the Gibbs diagram suggest that the source of water-soluble ions in the groundwater characterized by the freshwater type for both aquifers is the chemical weathering of the rock-forming minerals, while the chemical structure of the groundwater typical of the low-salinity type is mostly controlled by evaporation, anthropogenic activities (e.g., intensive and long-term irrigation, agricultural fertilization) and slightly by other processes, such as the chemical interaction between aquifer rocks and groundwater. In addition, salty paleowater and saltwater intrusion is the main source of the dissolved solids in the groundwater characterized by the high-salinity water type.

The SOM provided readily understandable and visualized results for classifying the hydrogeochemical groundwater data into exclusively distinguishable hydrogeochemical types. Therefore, the SOM was found to be a very effective tool for the assessment of groundwater quality in terms of the seasonal and spatial hydrogeochemical characteristics.

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CHAPTER 5

GENERAL CONCLUSIONS AND RECOMMENDATIONS

5.1 General conclusions

Groundwater is an important natural resource with high economic value and sociological significance in the RRD of Vietnam because water supply in the delta greatly depends on groundwater. In recent years, this delta has been faced with declining groundwater availability as well as deteriorating groundwater quality owing to the increased water demand and a concomitant increase in the amount and types of pollutants entering the hydrological cycle resulting from urban, industrial and agricultural development. Therefore, achieving sustainable management of groundwater is necessary to secure its future availability and ecological value.

To that end, this study investigates the hydrogeochemical properties of the groundwater on the basis of major ion chemistry with two main objectives: (1) to identify the spatio-seasonal hydrogeochemical characteristics of groundwater in the delta; (2) to determine the factors controlling the composition of groundwater. The findings of this study provide fundamental references for further groundwater analyses and management strategies in the RRD. To achieve these goals, the Piper diagram was used to investigate the hydrogeochemical facies, one of the most effective tools used to differentiate various forms of geochemical reaction, and then the Gibbs diagram was used as reference to determine the factors that govern groundwater composition. Finally, clustering spatio-seasonal hydrogeochemical data to assess the groundwater quality in the delta was carried out using self-organizing maps in combination with a hierarchical cluster analysis.

In this study, the spatial and seasonal changes in the hydrogeochemical facies of groundwater in the two main aquifers of the RRD were investigated by analyzing the physicochemical data obtained in 2011 from 31 conjunctive wells in the delta's Holocene unconfined aquifer and Pleistocene confined aquifer using the Piper diagram and the Gibbs diagram. Interpretation of hydrogeochemical analysis revealed that the concentrations of most ions are higher in the Holocene unconfined aquifer than in the Pleistocene confined aquifer throughout the year. The concentrations of almost all of the ions decrease from the dry to rainy seasons in both aquifers. Results from the Piper diagram show that the groundwater in both aquifers in the upstream area of the delta is dominated by the [Ca^{2+}-HCO_3^-] water type, while the [Na^+-Cl^-] dominates along the middle-stream and downstream areas. Seasonal changes in the hydrogeochemical facies in both aquifers, comparing the results for the dry and the rainy seasons, were detected in approximately one third of the sampling wells, which were mainly located at the upstream portion of the delta. The hydrogeochemical facies of Holocene aquifers were different from that of Pleistocene by about 45% of the sampling wells in both the dry and rainy seasons, which were found mostly in the upstream and middle-stream areas. The Gibbs diagram suggest that in Holocene unconfined aquifer, the natural mechanism controlling groundwater chemistry is the rock-water interaction in the upstream and southwest middle-stream areas, while marine activities, such as salty paleowater and saltwater intrusion, affect groundwater chemistry in the rest of the delta. In the Pleistocene confined aquifer, the source of the dissolved ions in the groundwater is rock-water interaction in the upstream and the southeast downstream area, but salty paleowater and saltwater from the sea are the main factors influencing groundwater chemistry in the middle-stream and northern downstream areas.

To assess groundwater quality in the delta, hydrogeochemical groundwater data comprising major ions from 47 Holocene unconfined and 52 Pleistocene confined wells that were obtained during the dry and rainy seasons in 2011 were classified using the self-organizing maps in combination with a hierarchical cluster analysis. From the results of the self-organizing maps for Pleistocene confined aquifer, the major ion chemistry data were divided into eight clusters, which basically revealed three representative water types: high salinity (three clusters), low salinity (three clusters) and freshwater (three clusters). The high-salinity types were located in the middle-stream and coastal areas of the RRD, while the low-salinity types were observed near the western and northeastern boundaries of the delta. Cluster changes from the dry to rainy seasons were detected in approximately one-third of the observation wells. The increase in groundwater recharge during the rainy season is the main reason for these changes. The self-organizing maps application classified the Holocene unconfined hydrogeochemical data into five clusters, which revealed three basic representative water types: high salinity (one cluster), low salinity (two clusters) and freshwater (two clusters). The spatial distribution of clusters and water types were identified. In particular, the low-salinity type was found not only in the downstream area but also in the northeastern parts of the upstream and middle-stream areas, where the groundwater was mainly classified into one specific cluster, in which agricultural activities were considered to influence groundwater chemistry. Cluster changes from the dry to rainy seasons were detected in approximately one-fifth of the observations wells. Dilution by surface water may significantly affect the chemical characteristics of the unconfined aquifer during the rainy season. Furthermore, Gibbs diagram was also created to elucidate the hydrogeochemical characteristics classified by the self-organizing maps. Based on Gibbs diagram, the source of soluble ions in the groundwater of the freshwater types was found to be the weathering of rock-forming minerals, while anthropogenic and marine activities (leaching from salty paleowater and salt water intrusion) were found to be the main factors affecting the chemistry of the groundwater characterized by the low- and high- salinity types, respectively. The findings about the classification of hydrogeochemical groundwater data will provide valuable insights into the spatio-seasonal hydrogeochemical characteristics of groundwater in the RRD.

5.2 Status of groundwater resources management

A literature review of available published materials and researches on groundwater provides some general conclusions on the status of groundwater resource management in the RRD as the following:

- In Vietnam, disparate state agencies are responsible for different aspects of groundwater management. For example, the ministry of health portal currently monitors groundwater quality as part of its regulation of public drinking water systems and administers local assistance grants for groundwater supply projects. The Ministry of Natural Resources and Environment monitors groundwater quality, issues permits for pollutant discharges that impact groundwater quality, oversees and helps fund the cleanup of groundwater contamination.

- Gaps in groundwater management complicate groundwater planning in the delta. Integrating nonstandardized and potentially conflicting data sources into supply projections is time-consuming and costly. Although the RRD has made great progress to address groundwater management through its Groundwater Monitoring Network, groundwater monitoring, exploration, and data gathering is still inadequate. More observation wells should be installed in the delta, especially in the rural and coastal areas. Systemwide coordination cannot easily be accomplished solely through local management because groundwater flows across political boundaries.
- Groundwater management links to integrated water resources management are not well established in both policy and practice. There is still a general bias towards groundwater resources for drinking water in the delta. More attention should be paid on surface water and rainwater as alternative sources of drinking water supply.
- There is a disconnection between groundwater law and science in Vietnam in general and the RRD in particular. Current law does not acknowledge the physical connection between groundwater and surface waters. Water rights are required only for withdrawals from surface waters, but hydrological science demonstrates that groundwater withdrawals impact surface waters and vice versa, potentially creating water rights conflicts.
- The performance in groundwater resource management in the RRD is still rated as “poor development”, compared to relevant international practice. Groundwater-related legislation in Vietnam including the RRD is still outdated, or even not yet

implemented for some provinces, while many countries already have modern integrated legislation.

- Lack of scientific analyses, public awareness on current situation of groundwater resources, and long-term planning for groundwater development are among the most problematic issues for sustainable groundwater management in the RRD.

5.3 Recommendations

Groundwater is a major contributor to water supply in the RRD, Vietnam. Improved management of groundwater resources is a key option for meeting future water demands (Anthony Rendon and Richard Bloom, 2014). In order to develop and manage groundwater resources in a sustainable for long-term water supply, some recommendations to prove groundwater management are proposed as the following:

- Monitoring of groundwater and surface water of water quality and of quantity are often performed by different authorities, so the resultant information needs to be assessed in combination.
- Effective management requires awareness of the status of groundwater, both its quality and the quantity available. It follows that monitoring is a prerequisite in order to identify whether problems are occurring or are likely to occur. Long-term data covering all key elements of the hydrological cycle including groundwater fluctuation, water-level trends, groundwater quality are essential as a basic for management and for evaluating the implications of changes in use. Therefore, continued support for basic data collection and groundwater evaluation is justified on both scientific and social process grounds.
- The availability and sustainability of water supplies in the RRD are influenced by many factors, one of which is groundwater quality. This groundwater quality assessment establishes a regional baseline against which groundwater quality conditions can be tracked over time and provides process-level understanding to help explain changes.

- Data access is probably one of the most important factors determining the ability of social auditor to press governments and society as a whole to address emerging problems and their social or environmental impacts. Therefore, continued support for the dissemination of national groundwater for groundwater users, where available, would seem a more appreciate direction to take.
- Water resources are interconnected through systems, including rivers, lakes, wetlands, and aquifers. The planning for utilization of water resources must be considered in the entire hydrological cycle composed of both groundwater and surface water. A sustainable groundwater development requires the adequate understanding of aquifer system, quantitative and qualitative monitoring of the resources, and the interaction with land and surface water development. The environmental services provided by groundwater, including base flows to rivers and wetlands, ought to be recognized and protected within an integrated planning framework.
- The main groundwater quality problems include: salinization, either from over-irrigation and waterlogging or saltwater intrusion, and groundwater contamination from on-site sanitation or poor well design, or construction. Assessment of the magnitude of these threats is necessary to the sustainability of groundwater resources. Possible contaminants should be controlled so that they cannot react with the groundwater system.
- Groundwater should be treated as both an economic and a social resource, and priced accordingly. In other words, groundwater pricing needs to be introduced based on the principle that water is an economic as well as a social good. Users need to be confronted with at least part of the full economic cost of groundwater.
- The essential requirement to achieve sustainable development of water resources is the recognition of environmental sustainability. In planning for groundwater development, short-term socio-economic gains may have to be traded with long-

term environmental sustainability. For environmental sustainability, the development and management of groundwater resources must pursue two main objectives: provision of water for beneficial uses at minimum cost, and avoidance of adverse effects on the environment.

5.4 Future works

Future research works may involve further study on:

- Further research focused on long-term groundwater quality trends under variable climate, land use and hydrogeochemical setting may further the understanding of the geochemical processes, hydrodynamics, and interactions between groundwater with aquifer materials and surface water.
- Further geophysical mapping of the distribution of groundwater salinity in combination with detailed surface and groundwater levels is likely to be the most effective means of determining groundwater flow paths and discharge/recharge zones to enable monitoring the fresh water-seawater interface. Monitoring of the interface, spatially and temporally, is required to protect this water resource against deterioration from saltwater intrusion.
- Further study on interaction of surface water and groundwater and impacts of climate change on groundwater resources would be a significant step for efficient and systematic approach to sustainable groundwater management in the RRD.
- Future work on feasibility of rainwater harvesting and recharge to groundwater resources in order to improve aquifer storage and recovery may further enhance the availability and sustainability of groundwater resources.

The expected findings from the above future research directions will be vital for the development of adaptive responses to groundwater problems and policy approaches towards sustainable development of groundwater resources in the RRD of Vietnam.

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APPENDIX

Table A-1 List of municipalities in the RRD of Vietnam

No.	City name	Provinces	City status	Area (km^2)	Population
1	Hanoi	Hanoi	1	3323	2,857,800
2	Hai Phong	Hai Phong	1	243	871,300
3	Nam Dinh	Nam Dinh	2	46	331,700
4	Hai Duong	Hai Duong	2	71	377,400
5	Thai Binh	Thai Binh	2	68	178,600
6	Bac Ninh	Bac Ninh	2	80	276,000
7	Ninh Binh	Ninh Binh	2	48	174,000
8	Bac Giang	Bac Giang	2	32	126,810
9	Vinh Yen	Vinh Phuc	2	51	232,800
10	Hung Yen	Hung Yen	2	47	144,200
11	Phu Ly	Ha Nam	2	34	82,400

Notes: (1) Centrally-controlled municipalities, (2) Provincial municipalities

Sources: General Statistics Office of Vietnam, 2012

Table A-2 Hydrogeochemical data of groundwater in Pleistocene confined aquifer in the Red River Delta

Well No	Season	TDS (mg/L)	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	NH_4^+ (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)
1	Dry	328	7.43	78.25	24.08	11.00	3.00	390.53	16.81	10.64	3	0.02	0
	Rainy	428	6.98	101.20	32.83	10.50	1.90	434.77	16.81	47.65	5	0	0
2	Dry	243	8.2	44.09	13.38	26.68	3.19	268.49	1.80	11.52	3.6	0.02	0
	Rainy	244	7.01	41.08	15.81	25.00	3.30	271.54	1.80	13.29	4	3.8	0.28
3	Dry	299	6.65	43.09	26.14	19.50	3.60	288.32	4.32	22.34	23	2.4	1.68
	Rainy	384	7.45	56.21	22.74	41.25	3.74	384.43	10.81	22.34	20.67	0.02	0
4	Dry	416	7.02	96.20	20.06	21.50	1.78	433.24	2.40	35.45	23	0	0
	Rainy	328	7.26	87.17	13.38	18.50	1.10	347.81	6.21	21.27	3.44	0	0
5	Dry	376	7.13	55.11	33.44	30.00	3.95	381.38	3.36	37.22	1	0	0
	Rainy	366	6.51	62.12	32.23	28.25	4.15	384.43	6.02	42.54	0	0.19	0
6	Dry	1145	7.72	60.70	41.91	299.50	8.90	479.01	30.02	467.94	16.55	0	0
	Rainy	1224	6.66	47.60	41.04	340.00	8.30	390.53	36.02	538.84	15	0	0
7	Dry	704	7.9	93.69	35.66	58.20	1.92	651.70	9.61	19.14	80	0	0
	Rainy	571	6.62	51.21	25.75	34.41	3.78	300.30	36.02	3.24	70.4	2.25	0
8	Dry	341	7.18	46.29	20.42	41.48	2.47	284.11	2.30	60.40	8.5	0.02	0
	Rainy	348	7.3	55.11	18.06	46.20	2.04	302.05	2.20	65.58	12.1		0
9	Dry	153	7.05	33.65	10.18	4.00	1.25	167.81	1.60	7.09	0	0.12	0.2
	Rainy	164	7.76	43.09	9.73	5.25	1.05	186.11	1.20	8.86	0.34	0	0
10	Dry	194	7.65	41.89	11.36	11.00	4.13	210.52	4.20	8.86	2.4	0.07	0
	Rainy	203	6.8	48.24	13.53	9.74	5.51	222.72	14.41	9.60	0.98	0	3.01

Well No	Season	TDS (mg/L)	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^{-} (mg/L)	SO_4^{2-} (mg/L)	Cl^{-} (mg/L)	NH_4^{+} (mg/L)	NO_2^{-} (mg/L)	NO_3^{-} (mg/L)
11	Dry	451	7.3	47.24	19.58	70.15	4.37	425.31	14.29	15.82	40	0	0
	Rainy	526	7.18	48.10	52.29	73.20	4.02	619.35	11.38	21.27	27.4	0.02	0
12	Dry	183	7.18	32.06	13.74	11.50	1.35	194.20	2.28	9.26	1.5	0.16	2
	Rainy	162	6.17	28.06	13.95	10.25	0.95	180.01	7.20	7.98	1.67	0	0
13	Dry	243	6.9	24.65	15.65	29.66	4.94	238.90	2.16	11.65	10	0	0
	Rainy	225	6.95	30.87	12.03	29.04	4.68	222.42	2.16	13.56	11.15	0.08	0
14	Dry	145	6.9	27.03	7.63	10.73	4.94	146.45	6.00	10.64	11		0
	Rainy	161	8.35	19.04	17.18	8.00	3.55	170.86	6.60	11.52	8	0.14	0
15	Dry	386	8.25	103.21	22.49	8.60	1.45	463.75	0.00	7.09	0.4	0	0
	Rainy	378	7.6	102.20	23.11	10.25	1.48	448.50	4.80	7.98	0.6	0	0
16	Dry	1055	7.5	74.15	71.13	165.00	11.90	146.45	456.29	186.11	0.5		0
	Rainy	345	7.07	15.03	13.98	86.00	3.80	88.48	14.41	162.18	0.35		0
17	Dry	856	6.77	92.69	53.20	160.00	5.30	250.18	12.01	475.03	20	0	0
	Rainy	886	8.31	82.67	44.08	165.00	4.65	308.15	18.01	386.41	20.6	0	0
18	Dry	2912	7.1	205.40	106.41	687.50	7.85	405.78	12.00	1637.80	40	1.98	0
	Rainy	3011	8.01	197.90	110.96	725.00	7.30	408.83	78.05	1641.34	39.8		0
19	Dry	493	7.04	77.15	31.62	51.00	6.10	433.24	4.80	67.36	6.4	18	1.8
	Rainy	465	7.33	43.34	22.86	93.73	5.15	369.17	0.00	102.80	14		0
20	Dry	1689	7.43	118.24	80.86	352.00	10.80	24.41	2.40	1070.59	26	0.03	0
	Rainy	1265	6.7	180.36	45.60	210.00	7.30	253.23	6.00	673.55	7		0
21	Dry	554	6.87	45.09	30.40	107.50	4.80	73.22	0.00	310.19	0.52	0.02	0
	Rainy	711	6.98	55.11	35.26	147.00	10.10	115.94	31.22	363.36	0.4	0.03	0

Well No	Season	TDS (mg/L)	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^{-} (mg/L)	SO_4^{2-} (mg/L)	Cl^{-} (mg/L)	NH_4^{+} (mg/L)	NO_2^{-} (mg/L)	NO_3^{-} (mg/L)
22	Dry	1058	5.87	105.21	42.56	195.00	12.50	283.74	236.15	304.87	0	0.02	4
	Rainy	995	6.8	143.29	43.47	8.92	2.93	221.05	136.75	198.52	2	0.05	0
23	Dry	3273	8.33	89.18	105.55	950.00	44.00	106.79	6.00	1985.20	6.5	13.6	0
	Rainy	3180	7.49	75.15	106.40	942.50	42.00	67.12	0.00	1949.75	7.5		0
24	Dry	10071	7.04	100.20	249.28	3300.00	82.00	15.26	0.00	6292.38	12.5	0.02	0
	Rainy	2363	7.27	78.01	97.06	651.52	25.80	15.40	0.00	1490.67	3.01		0
25	Dry	898	7.65	93.19	62.62	140.00	8.85	295.95	28.82	397.04	0.8	1	2.4
	Rainy	695	7.05	90.18	54.72	83.00	7.65	308.15	0.00	294.24	1.2	0	0
26	Dry	1931	6.6	175.55	135.04	600.00	197.50	35.61	0.00	1795.99	40		0
	Rainy	2978	7.23	110.22	72.05	306.45	8.01	18.31	0.35	907.52	2.15		0
27	Dry	757	7.34	54.11	40.73	155.00	6.35	18.31	9.61	464.40	0.92		0
	Rainy	738	7.34	55.11	45.60	139.50	6.65	21.36	0.00	460.85	2.2		0
28	Dry	1405	7.69	85.17	47.18	365.00	20.80	421.04	0.00	623.92	2.2	0.02	15.2
	Rainy	385	7.56	33.57	16.11	80.00	4.85	125.09	0.00	180.80	1.02	0.51	0
29	Dry	883	7.44	18.04	38.91	250.00	11.60	259.34	20.38	397.04	2	2.4	0
	Rainy	846	7.45	17.54	34.96	250.00	12.90	271.54	18.01	366.91	1.9	0.25	0
30	Dry	785	7.91	40.08	28.91	188.00	7.00	180.01	0.00	381.09	3.2	24	0
	Rainy	671	7.04	40.08	36.42	155.00	6.55	146.45	0.00	347.41	0		0.49
31	Dry	3962	7.5	127.76	134.67	1145.20	40.50	208.14	48.03	2277.75	0	14.95	0
	Rainy	562	7.75	39.85	32.06	123.15	5.81	280.69	1.20	198.52	0	0.58	0
32	Dry	237	7.4	28.06	13.37	34.00	1.35	210.52	16.31	25.70	0	0	0
	Rainy	206	7.26	27.05	13.38	32.50	1.75	198.32	2.42	24.82	0	0	0

Well No	Season	TDS (mg/L)	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^{-} (mg/L)	SO_4^{2-} (mg/L)	Cl^{-} (mg/L)	NH_4^{+} (mg/L)	NO_2^{-} (mg/L)	NO_3^{-} (mg/L)
33	Dry	112	7.35	3.08	6.58	23.10	5.25	104.35	3.78	4.79	7.5	0.12	0
	Rainy	683	7.51	60.62	78.25	5.78	5.12	626.98	1.73	9.97	54	0.05	0
34	Dry	311	7.35	31.68	8.68	67.73	2.30	262.39	1.60	50.52	2.15	0	0
	Rainy	278	7.53	33.07	10.33	57.00	1.85	210.52	16.81	49.63	2.32	0.09	0
35	Dry	274	7.2	44.10	32.58	50.00	9.18	341.71	4.80	61.15	0.2	0.03	0
	Rainy	270	7.25	49.10	27.97	53.00	8.50	360.02	4.83	47.86	0.43	0	0
36	Dry	256	7.36	16.35	10.55	60.18	2.91	201.37	2.40	50.52	1.3	0	0
	Rainy	251	7.2	22.04	9.12	60.00	2.45	198.32	3.62	50.52	1.6	0	0
37	Dry	141	7.36	10.62	5.80	29.42	2.33	140.53	2.26	7.50	0	0	0
	Rainy	131	7.15	8.27	7.45	30.00	1.90	140.35	1.20	9.75	0	0	0
38	Dry	219	6.4	38.08	8.51	27.25	3.60	228.83	4.80	5.32	0	0	1.2
	Rainy	179	8.18	10.94	10.94	37.50	2.85	192.21	6.01	6.20	0	0.7	0
39	Dry	183	7.49	35.57	7.36	16.75	2.05	167.81	0.00	23.93	0.48	0.07	
	Rainy	173	8.24	29.31	7.14	23.75	2.50	131.19	3.61	38.11	0	1.76	0.3
40	Dry	66	6.24	6.01	3.04	7.25	3.15	45.77	0.60	9.75	0		6.4
	Rainy	55	7.44	5.76	3.19	7.00	2.95	30.51	6.01	12.41	0		0
41	Dry	246	8	44.09	15.81	18.40	1.85	231.88	7.20	28.36	0.44	0.07	0.8
	Rainy	218	7.37	40.08	15.81	17.80	1.48	213.57	4.80	27.47	0.96	0	0
42	Dry	251	8.38	47.34	12.13	23.10	2.15	189.16	0.00	61.15	3.6	0.07	0
	Rainy	252	7.86	44.74	12.13	19.00	2.19	158.65	24.02	24.02	4.04	0.06	0
43	Dry	98	7.46	7.10	4.63	16.80	3.41	42.71	4.21	32.79	0	0.04	1.2
	Rainy	71	7.98	6.31	3.05	13.13	2.99	39.66	0.81	23.04	0	0	0

Well No	Season	TDS (mg/L)	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	NH_4^+ (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)
44	Dry	115	6.96	16.26	7.26	10.18	2.26	72.47	1.14	31.15	0		0
	Rainy	74	7.37	9.52	4.26	9.50	1.75	51.87	3.61	16.84	0		0
45	Dry	561	6.95	21.04	22.50	155.00	9.60	265.44	18.42	175.48	0		0
	Rainy	511	7.8	14.03	13.71	143.00	11.40	241.03	3.61	168.39	0	5.2	0.48
46	Dry	388	7.06	27.05	10.95	90.00	5.70	91.53	19.21	177.25	0	0.02	0
	Rainy	338	6.89	26.05	10.34	80.00	6.35	100.68	1.02	155.09	0		0
47	Dry	174	7.28	19.84	9.41	36.00	2.12	68.46	0.00	69.60	0.34	0	0
	Rainy	153	7.8	14.28	7.30	31.50	3.20	94.58	0.60	45.20	0	0.16	
48	Dry	198	7.65	21.04	16.58	24.25	2.30	195.26	1.50	23.04	0	0	0
	Rainy	163	6.98	19.04	14.89	19.50	1.75	149.50	4.80	19.50	0	0.05	0.22
49	Dry	160	7.42	22.09	10.86	19.95	1.68	176.96	2.40	6.20	0.8	0.02	0
	Rainy	143	7.89	21.04	9.12	19.50	1.10	155.60	2.40	8.86	1.6	0.1	0
50	Dry	298	8.19	44.53	19.45	31.00	3.20	286.79	22.57	21.27	0	0.1	1
	Rainy	236	7.27	45.09	17.63	19.50	2.00	265.44	4.80	9.75	0.3	0.02	0
51	Dry	1971	7.66	67.64	86.64	537.00	11.90	198.32	96.06	1052.87	1	0.02	0
	Rainy	1971	7.88	62.63	89.68	528.00	9.60	201.37	72.05	1036.91	2.16		0
52	Dry	814	8.47	72.65	57.82	150.00	6.90	729.19	18.01	125.85	4.6	0	0
	Rainy	791	7.9	41.08	62.63	164.75	7.66	668.17	0.00	136.80	13.1	21.1	2.75

Table A-3 Hydrogeochemical data of groundwater in Holocene unconfined aquifer in the Red River Delta.

Well No	Season	TDS (mg/L)	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	NH_4^+ (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)
1	Dry	659	7.17	126.25	33.44	58.40	19.00	540.03	33.62	102.81	0.56	0.1	0
	Rainy	678	7.45	137.27	31.01	70.00	11.40	610.20	19.21	101.03	5.72	0.07	0
2	Dry	485	6.73	84.17	27.43	55.20	1.35	326.46	1.44	134.71	30	0.3	0
	Rainy	546	7.14	62.23	20.79	73.80	0.99	322.18	1.44	110.61	28.6	0.06	0
3	Dry	1510	8	162.83	92.72	215.00	22.50	610.20	308.21	333.23	20	5	1
	Rainy	1245	7.65	133.27	60.19	218.00	23.80	808.52	94.88	280.06	23	0.1	0
4	Dry	418	6.95	105.81	20.47	23.65	1.85	433.24	2.40	37.22	10	0.02	0
	Rainy	358	7.36	83.77	23.41	14.30	1.75	382.90	6.21	35.45	10.6	0.03	0
5	Dry	362	6.71	56.11	32.83	24.50	3.95	366.12	2.40	46.97	1	0.02	0
	Rainy	338	7.44	54.11	34.05	25.00	3.55	338.66	1.78	46.09	1.14	0.23	0
6	Dry	395	6.74	72.14	19.94	10.20	3.64	219.68	39.63	31.91	6.5	0.75	2.56
	Rainy	399	7.39	89.18	27.36	14.75	4.15	442.09	23.78	5.58	11.25	0	0
7	Dry	660	7.4	102.41	39.16	67.20	7.70	715.92	6.84	23.58	80	0.02	0
	Rainy	594	7.17	96.19	36.12	53.40	4.98	617.37	5.70	28.62	53.6	0.05	0
8	Dry	319	6.74	46.90	27.61	50.40	1.50	318.84	2.42	60.45	2.5	0	0
	Rainy	165	7.39	20.79	9.73	25.25	0.60	143.40	3.00	25.70	2.94	2	0
9	Dry	116	6.98	31.14	4.59	3.50	1.43	125.09	5.28	6.20	0	0.32	0
	Rainy	133	7.85	36.08	7.60	3.80	1.05	149.50	9.61	7.09	0	0.02	0
10	Dry	393	6.72	88.18	21.89	18.50	1.80	387.48	21.01	26.59	0	12	4
	Rainy	398	8	90.18	27.97	20.00	2.20	411.89	14.41	30.13	0	0.09	3.6

Well No	Season	TDS (mg/L)	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	NH_4^+ (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)
11	Dry	270	7.52	37.07	21.28	26.80	3.05	213.57	16.81	44.31	0.7	0	0
	Rainy	242	7.85	42.08	17.63	23.10	2.60	207.47	14.23	33.68	0	0.9	0
12	Dry	228	6.74	24.07	22.74	15.40	0.80	197.70	9.61	18.61	0	0	0
	Rainy	205	7.63	33.07	19.94	14.05	0.84	219.67	2.40	21.27	0.61	0.14	0
13	Dry	531	7.76	72.94	33.20	52.00	8.26	521.72	4.32	28.72	60	1.1	0.4
	Rainy	619	7.4	56.11	68.40	42.50	5.55	645.29	1.20	29.91	36	9.2	0.2
14	Dry	632	7.16	175.35	24.93	15.25	0.85	502.19	93.66	56.72	0	0.04	3.04
	Rainy	478	7.54	139.28	16.41	15.50	1.75	414.94	65.40	31.02	0	0.07	0
15	Dry	671	6.96	162.32	29.19	49.00	7.50	662.07	2.40	76.22	1.3	0	0
	Rainy	652	7.05	159.32	30.40	45.50	4.85	619.35	12.01	84.19	2.16	0	0
16	Dry	1703	7.04	95.19	126.46	258.00	18.00	189.16	946.19	145.35	0.34	0	0
	Rainy	1323	7.44	90.18	133.76	135.00	19.60	204.42	685.58	150.66	0	1.05	0
17	Dry	558	7.55	99.20	31.01	57.00	0.85	402.73	76.25	77.10	0	0.36	2.65
	Rainy	512	7.88	96.19	27.36	59.00	0.70	433.24	50.24	58.49	0.88	0	0
18	Dry	475	7.5	59.52	26.75	68.75	7.76	414.94	0.00	83.31	24	0	0
	Rainy	423	7.34	66.13	24.75	45.54	6.99	384.43	19.21	46.97	16.6	0.02	0
19	Dry	440	7.6	102.81	21.52	28.50	3.10	433.24	6.22	34.56	0	15	0.4
	Rainy	435	7.5	94.19	28.57	23.90	4.75	485.11	1.20	25.70	7.5	0	0
20	Dry	520	7.3	104.21	30.40	35.00	6.20	491.21	0.00	42.54	3.2	30	0.6
	Rainy	519	7.9	109.42	32.83	25.50	7.35	509.52	7.20	62.92	13.5	0.02	0
21	Dry	2368	7.16	57.62	62.32	746.00	19.40	414.94	48.03	1159.22	0	26	0
	Rainy	855	7.8	35.07	30.40	240.00	9.90	311.20	48.03	327.91	0.68	0.27	0

Well No	Season	TDS (mg/L)	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	NH_4^+ (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)
22	Dry	1326	7.1	110.22	120.14	190.00	6.50	57.97	0.00	850.80	2.4	0.02	0
	Rainy	1475	6.5	118.24	123.42	242.50	7.65	82.38	2.40	918.84	2.4	0.03	0
23	Dry	5801	7.39	70.14	228.00	1750.00	80.00	1217.35	0.00	2977.80	12.5	48	5.6
	Rainy	5065	7.97	70.14	209.76	1500.00	60.50	887.84	36.02	2703.06	20	1.68	0.6
24	Dry	4761	7.41	190.38	114.06	1437.50	28.00	350.87	6.00	2782.83	3.4	1.5	0
	Rainy	809	7.68	124.25	37.09	130.00	5.70	527.82	3.21	240.17	0.4	0	0
25	Dry	578	6.54	21.04	32.23	132.00	10.00	216.62	78.46	177.25	0.44	0	0
	Rainy	519	6.72	32.06	21.89	120.00	9.70	189.16	86.45	146.23	2.05	0	0
26	Dry	4616	7.24	35.07	130.72	1500.00	64.00	945.81	6.00	2348.56	5.5	24	6
	Rainy	5895	8.11	20.04	179.36	1980.00	68.00	1238.71	0.00	2995.53	18.5	8.8	0.4
27	Dry	3273	7.4	90.18	243.20	775.00	46.50	610.20	6.00	1754.78	0.66	36	0
	Rainy	2993	7.64	152.30	213.71	574.75	38.48	665.12	34.82	1267.34	2.82	7.68	0
28	Dry	769	8.1	66.13	37.70	160.00	13.60	451.55	0.00	255.74	1.2	10	1.2
	Rainy	735	7.84	60.12	39.52	162.50	11.10	454.60	6.08	216.25	2.14	7.12	0.2
29	Dry	1640	7.7	60.12	60.80	426.00	34.50	591.89	0.00	700.14	10	3	0
	Rainy	1145	7.62	57.62	31.92	310.00	33.00	506.47	24.01	418.31	9.35	0	0.32
30	Dry	7212	8	90.18	252.32	2240.00	81.00	1199.04	24.01	3864.05	26	15	3.36
	Rainy	3016	7.95	97.70	116.12	835.50	20.05	237.98	48.03	1738.82	25.15	1.1	0
31	Dry	7206	7.3	142.79	223.44	2240.00	87.00	482.06	18.01	4200.83	11	26	0
	Rainy	6576	7.49	130.26	212.80	2050.00	89.00	448.50	0.00	3855.19	2.04	0	0
53	Dry	371	8.35	41.28	34.44	36.05	1.13	326.46	2.40	57.61	7.75	0.13	0
	Rainy	319	7.52	65.28	25.99	39.90	0.90	292.90	2.40	57.61	4.3	0.1	0

Well No	Season	TDS (mg/L)	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^{-} (mg/L)	SO_4^{2-} (mg/L)	Cl^{-} (mg/L)	NH_4^{+} (mg/L)	NO_2^{-} (mg/L)	NO_3^{-} (mg/L)
54	Dry	396	7.02	100.20	25.54	6.75	1.35	448.50	9.61	10.64	0	4.8	1.08
	Rainy	318	8.32	90.18	18.24	6.30	1.25	320.36	8.61	11.52	0	0	1.12
55	Dry	306	7.5	73.15	20.06	7.00	0.60	314.25	21.61	15.07	0	0	0
	Rainy	283	8.4	57.11	20.67	20.75	0.40	198.32	2.40	65.58	0	0	0.34
56	Dry	365	7.5	93.92	23.80	6.44	2.42	439.34	10.00	9.75	2.4	0	0
	Rainy	335	7.23	91.18	20.67	6.50	2.15	396.63	8.00	10.64	2.8	0.4	0
57	Dry	803	7.03	107.21	69.31	30.50	5.35	73.22	505.89	30.13	0.24	0.08	0
	Rainy	670	6.8	102.20	51.07	28.75	6.10	115.94	386.64	33.68	0.36	0	0
58	Dry	516	6.99	113.23	38.30	21.25	5.55	582.74	2.40	26.59	3.5	3.6	0
	Rainy	493	7.57	113.23	38.91	14.00	4.60	552.23	2.40	26.59	6.1	4.6	0.2
59	Dry	390	7.85	91.18	11.55	30.50	7.50	390.53	7.20	35.45	0	0	4
	Rainy	396	7.59	98.20	13.37	21.50	7.95	402.73	6.02	34.56	0	0.1	0.51
60	Dry	4319	7	37.58	94.30	1425.00	45.00	408.83	186.12	2295.39	0.34	10.4	0.46
	Rainy	8135	5.9	42.59	162.64	2800.00	62.00	70.17	276.17	4741.44	7	0	0
61	Dry	653	7.64	85.17	29.18	105.00	9.50	430.19	45.63	122.30	2.6	27.2	0.2
	Rainy	535	7.75	124.48	35.00	14.65	4.90	625.46	7.20	14.18	18	0.06	0
62	Dry	391	7.85	75.15	25.54	34.50	2.50	408.83	0.00	32.79	0	0.02	4
	Rainy	443	7.9	98.20	29.18	31.50	2.25	491.21	7.20	23.93	0.68	0.05	0
63	Dry	23759	8.31	97.70	91.26	450.00	18.20	750.55	150.09	629.24	0	24	3.4
	Rainy	20135	7.94	90.18	60.80	192.00	12.82	509.52	30.04	345.64	0	0.42	0
64	Dry	6702	6.46	90.18	150.54	1225.00	59.00	1107.51	156.10	1843.40	0.52	12.8	0
	Rainy	6828	7.47	145.29	94.24	655.00	50.00	735.29	300.19	957.15	5	0.08	0

Well No	Season	TDS (mg/L)	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	NH_4^+ (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)
65	Dry	1848	8.32	280.56	1076.16	6800.00	272.50	1289.35	1753.10	12868.35	0	3	1.2
	Rainy	996	7.62	210.24	741.76	6300.00	229.00	1372.95	1332.83	11609.88	0.52	0.08	0
66	Dry	2961	8	20.04	85.12	950.00	52.00	805.46	24.01	1364.83	6	32	6.4
	Rainy	2578	8.03	15.03	82.08	975.00	41.50	851.23	132.08	1285.06	9.3	8.3	0.3
67	Dry	4172	8.2	120.24	291.84	1850.00	84.00	546.13	852.53	3192.27	6.4	14	3.6
	Rainy	20883	7.41	95.19	322.24	1925.00	78.00	591.89	189.72	3500.69	0	0	0.2
68	Dry	13368	7.9	75.15	644.48	7200.00	250.00	826.82	0.00	13391.24	4.8	22	0
	Rainy	2978	8.24	48.98	555.56	5865.00	231.63	786.50	26.42	9464.18	53.2	1.1	0

Table A-4 Ranges of chemical parameters in Pleistocene confined aquifer in Hanoi and their comparison with the Vietnamese standards for drinking water.

Chemical parameter	Concentrations of ions				WHO standard value (maximum limit)	Vietnamese standard value (maximum limit)	Sample numbers exceeding maximum limit value	
	Dry season		Wet season				Dry season	Wet season
	Range	Mean	Range	Mean				
pH	6.5-8.2	7.2	7-7.9	7.5	-	6.5-8.5	none	none
TDS (mg/L)	153-1145	390	162-1224	398	-	1000	none	none
Ca^{2+} (mg/L)	24.65-96.2	53.7	28.06-101.2	53.8	-	-		
Mg^{2+}(mg/L)	10.18-41.91	22	9.73-52.29	23.33	-	-		
Na^{+} (mg/L)	4-299.5	48.78	5.25-340	51.67	200	200	6	6
K^{+} (mg/L)	1.25-8.9	3.4	0.95-8.3	3.4	-	-		
HCO_3^- (mg/L)	167.81-814.62	339.5	100.1-619.35	326.7	-	-		
SO_4^{2-}(mg/L)	1.6 -30.02	7.32	1.2-36.02	11.71	500	250	none	none
Cl^- (mg/L)	7.09-467.94	55.18	3.24-538.84	62.77	250	250	6	6
CO_3^{2-}(mg/L)	0.000-0.0026	0.0006	0.000-0.001	0.0005	-	-		
NH_4^+ (mg/L)	0-80	16.35	0-70.4	13.17	-	1.5	1, 2, 3, 4, 6, 7, 8, 10, 11, 12, 13	1, 2, 3, 4, 6, 7, 8, 11, 12, 13
NO_2^- (mg/L)	0-2.4	0.22	0-3.8	0.53	50/total nitrogen	3	none	2
NO_3^- (mg/L)	0-2	0.3	0-3.01	0.25		50	none	none
TH (mg/L)	120-340	212	115-388	231	-	300	4,6, 7	1, 7, 11

Table A-5 Ranges of chemical parameters in Holocene unconfined aquifer in Hanoi and their comparison with the Vietnamese standards for drinking water.

Chemical parameter	Concentrations of ions				WHO standard value (maximum limit)	Vietnamese standard value (maximum limit)	Sample numbers exceeding maximum limit value	
	Dry season		Wet season				Dry season	Wet season
	Range	Mean	Range	Mean				
pH	6.7-8.0	7.1	7.1-8.0	7.5	-	6.5-8.5	none	none
TDS (mg/L)	116-1510	488	133-1245	455	-	1000	3	3
Ca^{2+} (mg/L)	24.07-162.83	77.7	20.79-137.27	71.9	-	-		
Mg^{2+}(mg/L)	4.59-92.72	30.6	7.6-68.4	29.6	-	-		
Na^{+} (mg/L)	3.5-215	47.8	3.8-218	45.9	200	200	3	3
K^{+} (mg/L)	0.8-22.5	5.9	0.6-23.8	4.9	-	-		
HCO_3^{-} (mg/L)	125.09-753.6	383	143.4-808.52	407.6	-	-		
SO_4^{2-}(mg/L)	1.44-308.21	34.9	1.2-94.88	15.2	500	250	3	none
Cl^{-} (mg/L)	6.2-333.23	69	6.2-280.06	58.1	250	250	3	3
CO_3^{2-}(mg/L)	0.000-0.003	0.0006	.000-0.002	0.0008	-	-		
NH_4^{+} (mg/L)	0-80	16.3	0-53.6	13.3	-	1.5	2, 3, 4,6, 7, 8, 13	1, 2, 3, 4,6, 7, 8, 13
NO_2^{-} (mg/L)	0-5	1.5	0-9.2	1	50/total nitrogen	3	3	13
NO_3^{-} (mg/L)	0-4	0.6	0-3.6	0.3		50	none	None
TH (mg/L)	90-788	299	92-580	296	-	300	1,3,4,6, 10	1, 3, 6, 7, 10

Table A-6 Water types of groundwater samples in HUA and PCA

Sampling wells	HUA		PCA	
	Dry season	Rainy season	Dry season	Rainy season
1	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}- HCO_3^-]
2	[Ca^{2+}-HCO_3^-]	[Na^+-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
3	[Na^+-HCO_3^-]	[Na^+-HCO_3^-]	[Mg^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
4	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
5	[Ca^{2+}-HCO_3^-]	[Mg^{2+}-HCO_3^-]	[Mg^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
6	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Na^+-Cl^-]	[Na^+-Cl^-]
7	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]$_3$	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
8	[Ca^{2+}-HCO_3^-]	[Na^+-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
9	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
10	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
11	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Na^+-HCO_3^-]	[Mg^{2+}-HCO_3^-]
12	[Mg^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]	[Ca^{2+}-HCO_3^-]
13	[Ca^{2+}-HCO_3^-]	[Mg^{2+}-HCO_3^-]	[Na^+-HCO_3^-]	[Ca^{2+}-HCO_3^-]

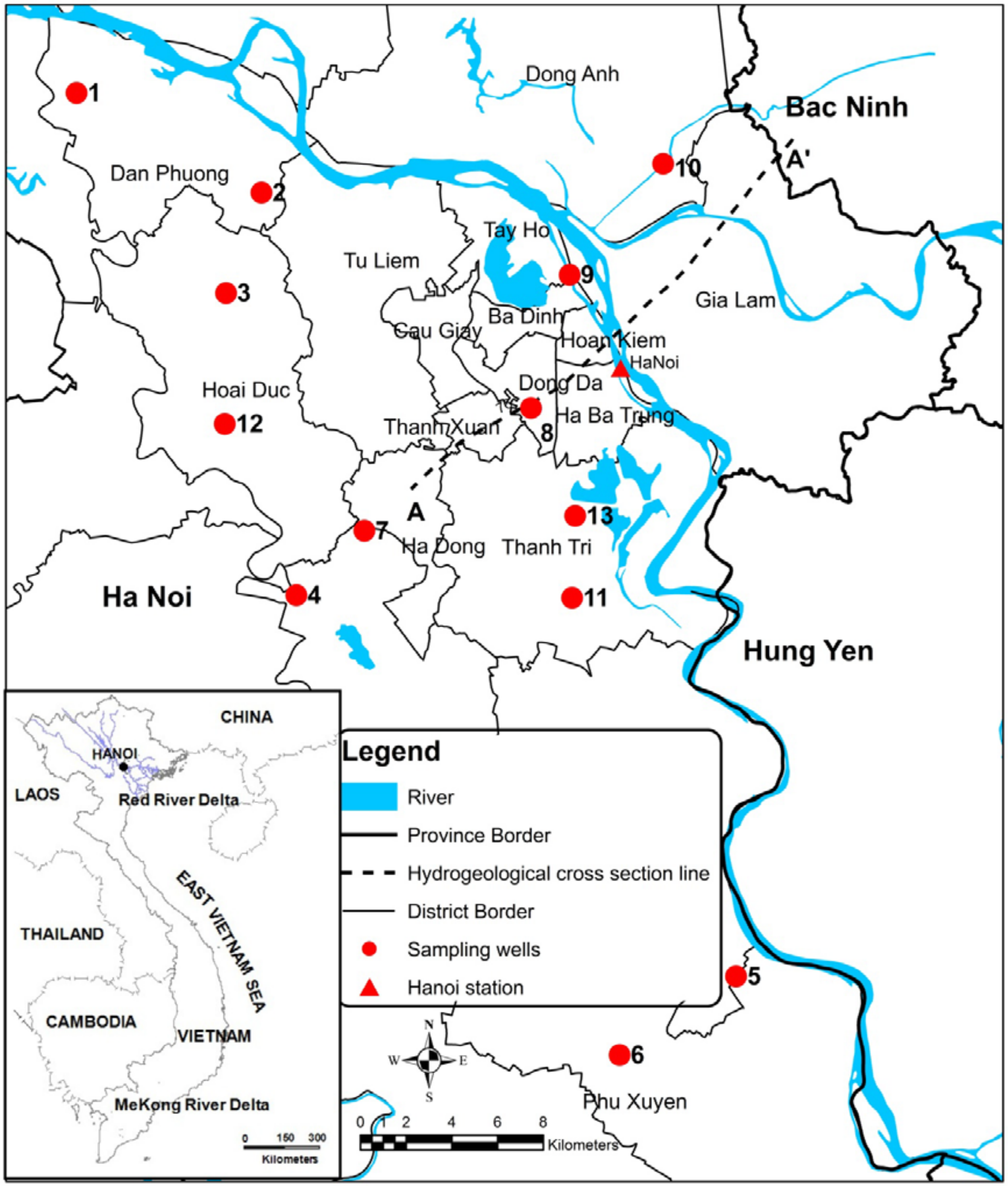
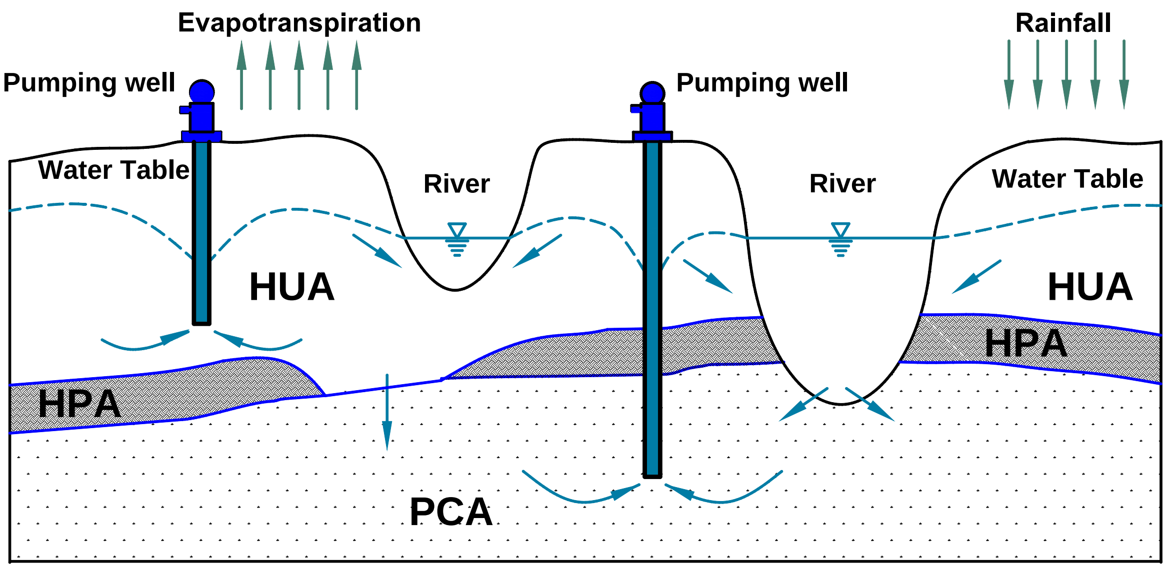


Fig. A-1 Hanoi and distribution of sampling points in Hanoi

a) Dry Season



b) Rainy Season

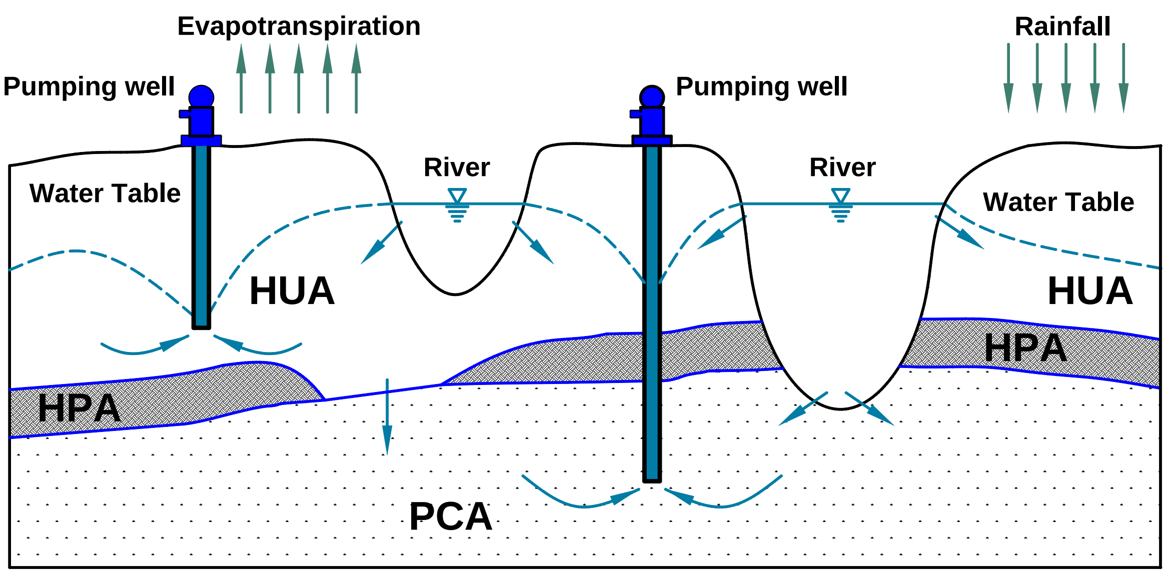


Fig. A-2 Schematic diagram showing the inflow and outflow to the groundwater system in Hanoi: a) for dry season, b) for rainy season

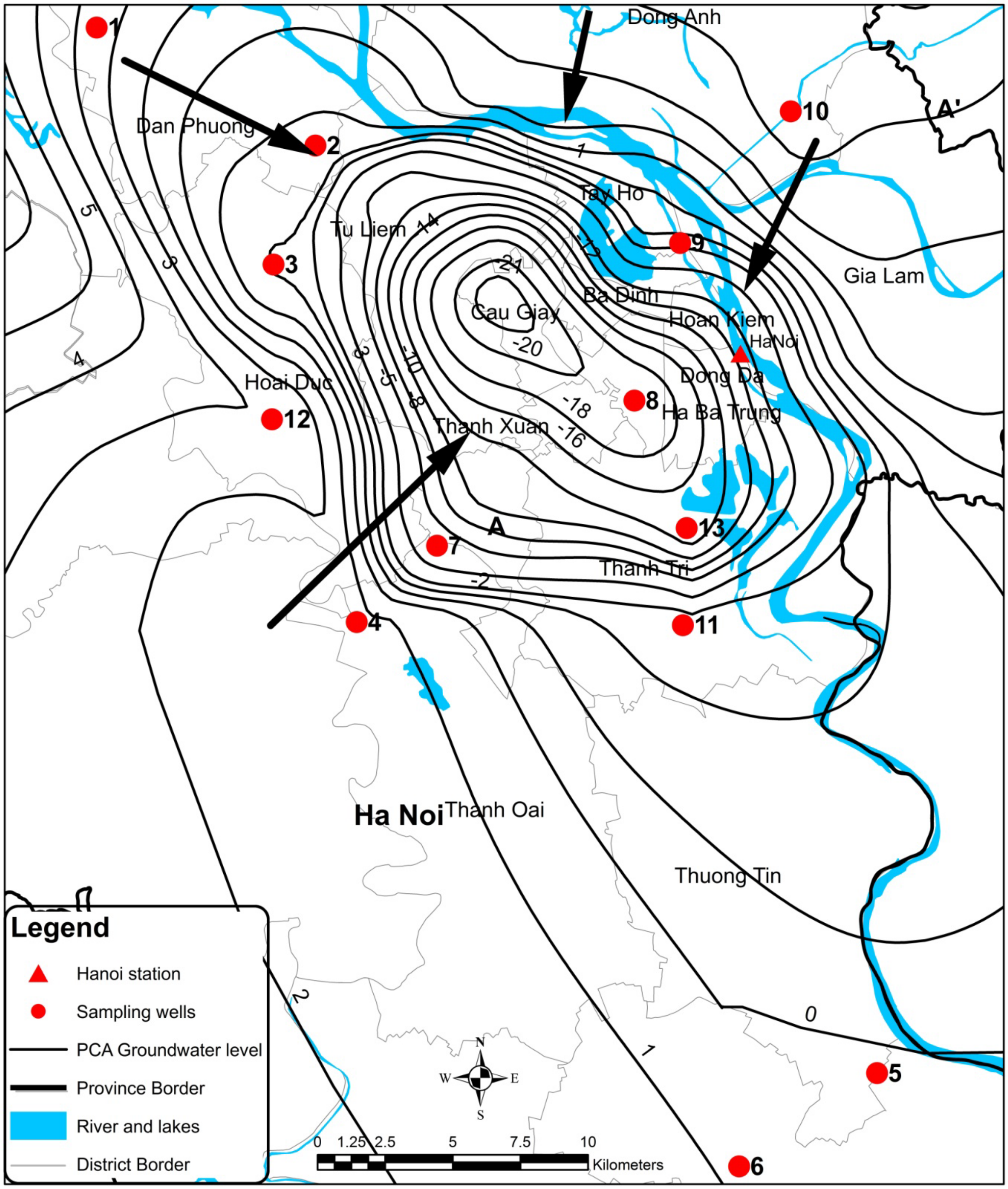


Fig. A-3 The annual average groundwater levels and flow directions for PCA

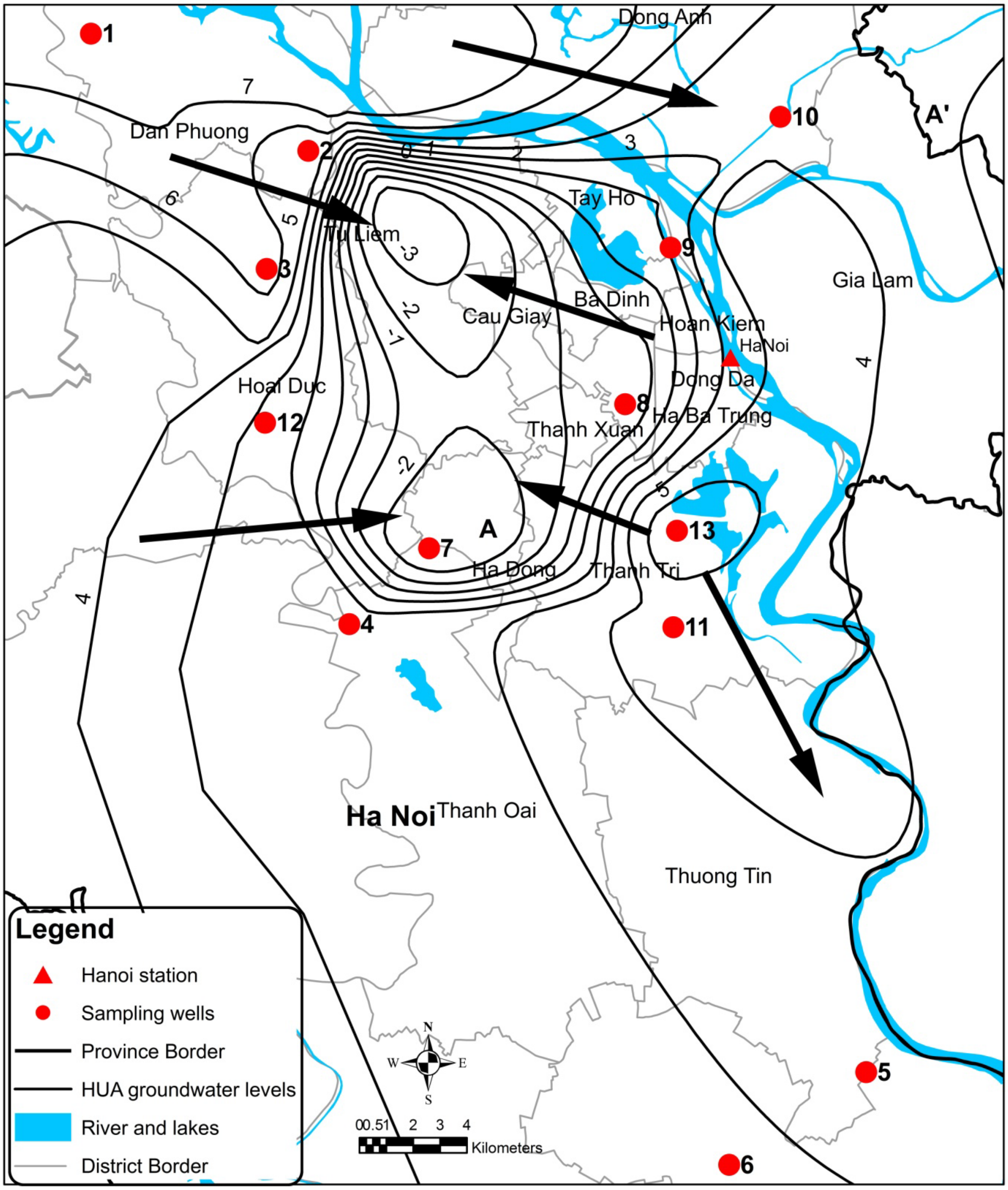


Fig. A-4 The annual average groundwater levels and flow directions for HUA

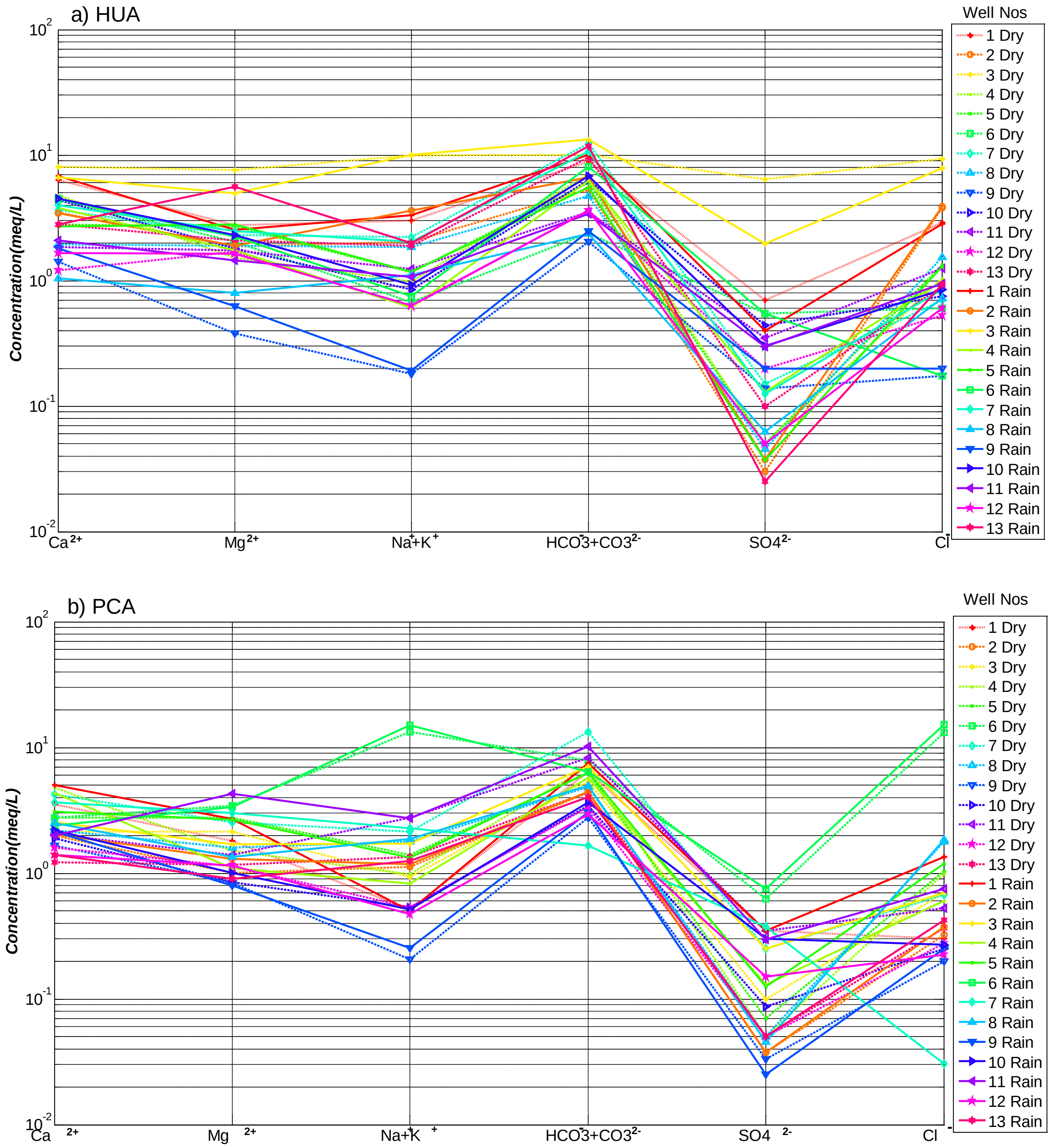


Fig. A-5 Schoeller diagram showing the hydrogeochemical composition of groundwater: a) for HUA, b) for PCA

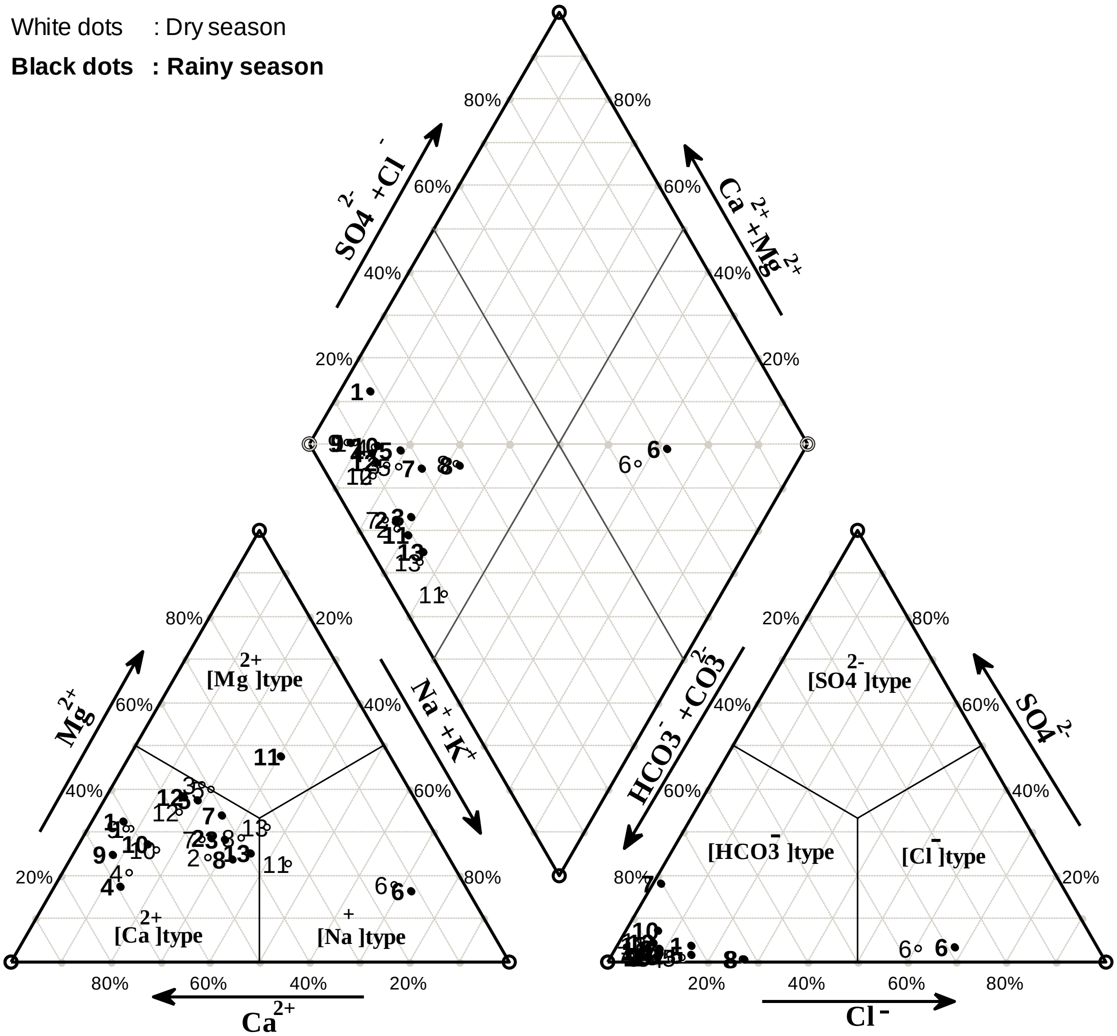


Fig. A-6 Piper diagram for Pleistocene confined groundwater in Hanoi

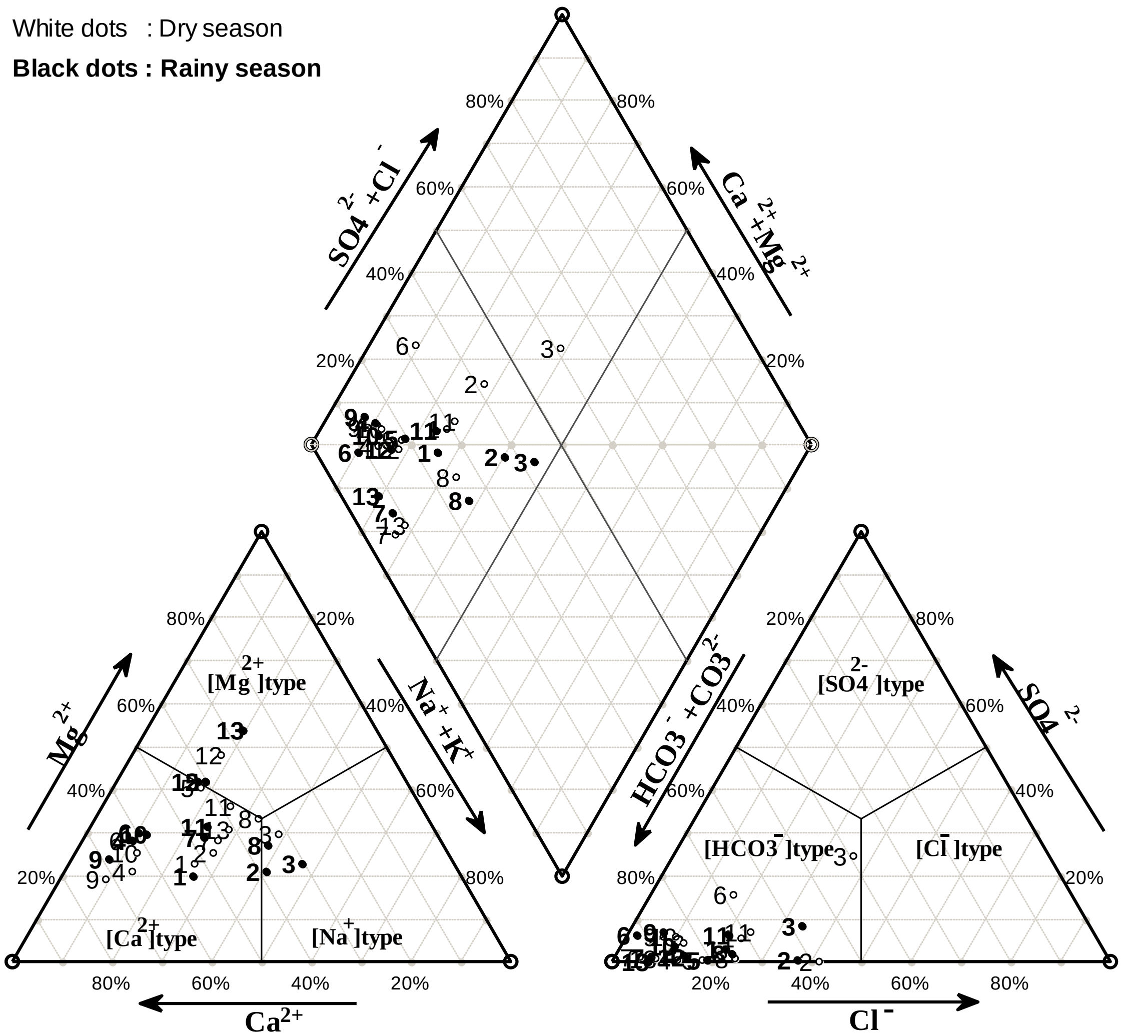


Fig. A-7 Piper diagram for Pleistocene confined groundwater in Hanoi

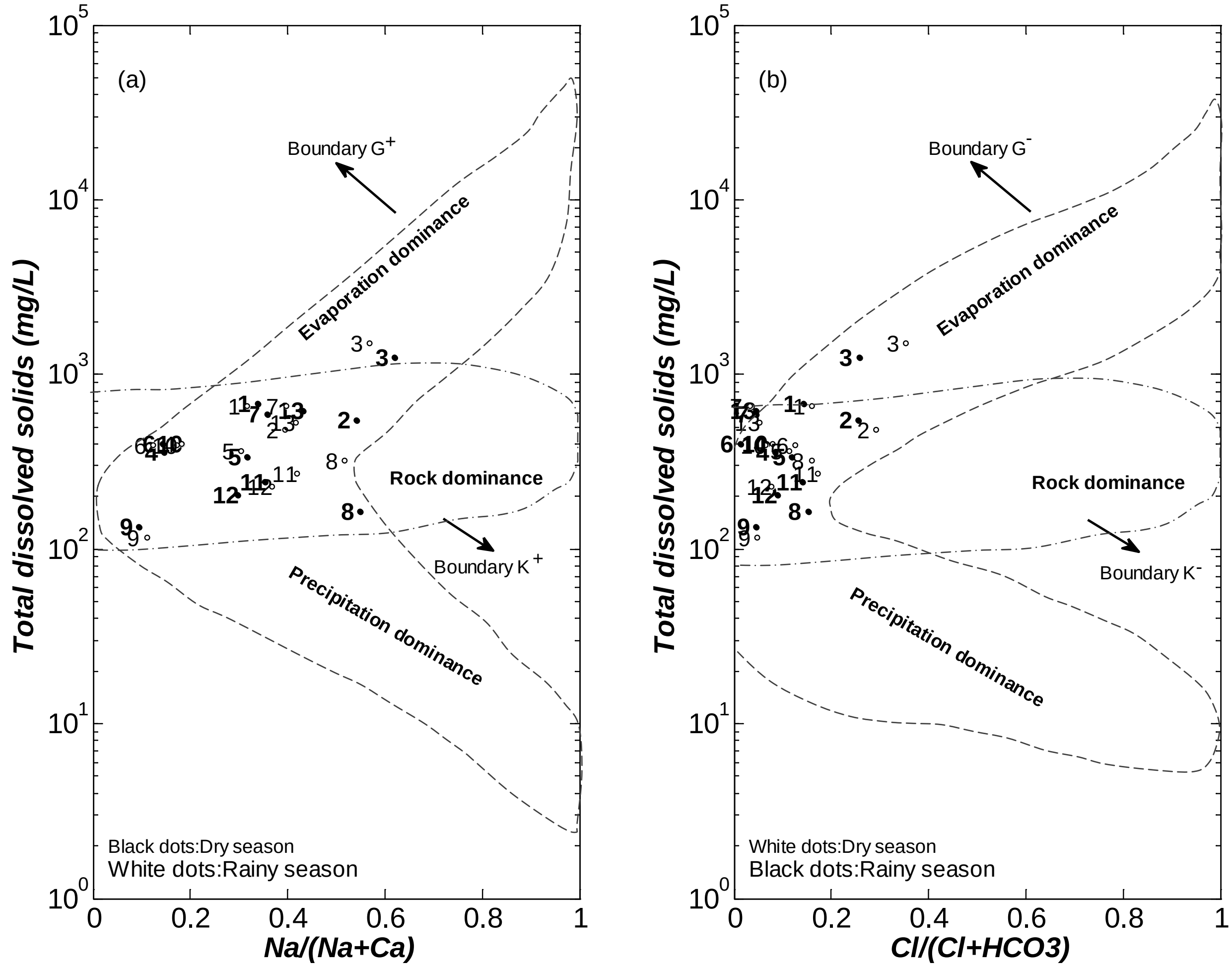


Fig. A-8 Gibbs diagram for Pleistocene confined groundwater in Hanoi: (a) Gibbs cation diagram, (b) Gibbs anion diagram

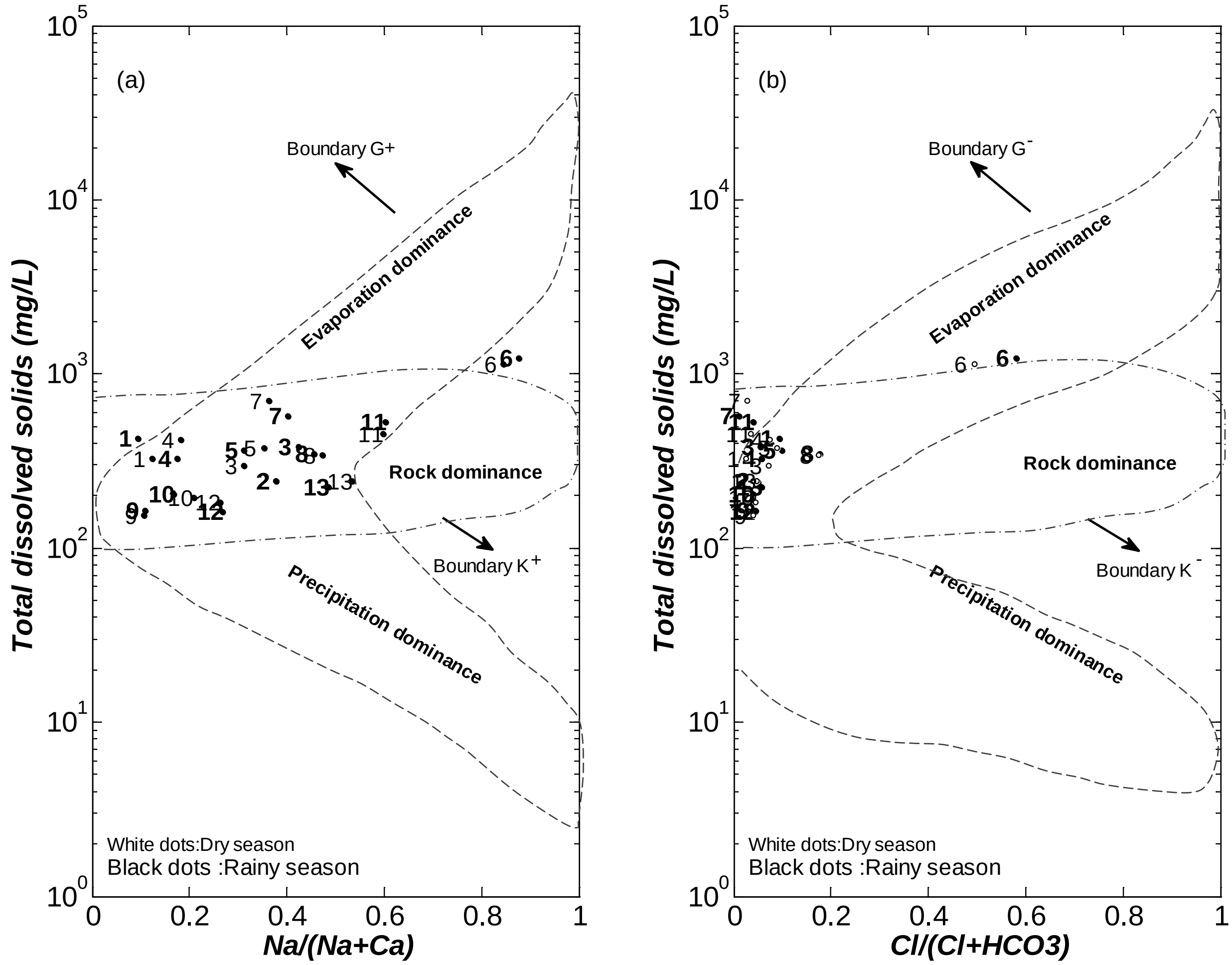


Fig. A-9 Gibbs diagram for Holocene unconfined groundwater in Hanoi: (a) Gibbs cation diagram, (b) Gibbs anion diagram