



Hydrogeochemical characteristics of groundwater from the two main aquifers in the Red River Delta, Vietnam



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ABSTRACT

In the Red River Delta, situated in the northern part of Vietnam, nearly its entire population depends solely on groundwater for daily water consumptions. For this reason, groundwater quality assessments must be carefully carried out using hydrogeochemical properties, to ensure effective groundwater resource planning for the Delta's present and future groundwater use. In this study, 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 obtained in 2011 from 31 conjunctive wells in the Delta's Holocene unconfined aquifer (HUA) and Pleistocene confined aquifer (PCA) using the Piper diagram and the 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, comparing the results for the dry and the rainy seasons, were detected in about one third of the sampling wells, which were mainly located at the upstream portion of the Delta. The hydrogeochemical facies of HUA were different from that of PCA by about 45% of the sampling wells in both the dry and the rainy seasons, which were found mostly in the upstream and middle-stream areas.

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1. Introduction

The Red River Delta (RRD) is the second largest delta in Vietnam with an area of about 13,000 km² 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; Montangero 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

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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 diagram 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.

2. Study area

Fig. 1 shows the geographical locations of the RRD and the 31 conjunctive groundwater sampling wells for both HUA and PCA. For convenient investigation of the study area, the RRD is divided into 3 parts: upstream, middle-stream and downstream areas by two hydrogeological cross-sections (lines A-A' and B-B') as shown in Fig. 1. Well Nos. 1–15 are in the upstream area, Well Nos. 16–24 are in the middle-stream area, and Well Nos. 25–31 are in the downstream area. The RRD is the most developed region in Vietnam and is comprised of 11 provinces/cities (Fig. 1). Two of Vietnam's major economic centers, Hanoi and Hai Phong, are located in the RRD (Bui et al., 2012).

The RRD is situated in the tropical monsoonal region with two distinct seasons: the rainy (May to October) and the dry (November to April) seasons. The annual average rainfall is about 1,600 mm, 75% of which occurs during the rainy season. The annual average humidity is about 80%, and the average temperature is 24 °C. The annual evaporation average is around 900 mm. The river network is quite extensive, with a network density of about 0.7 km/km² (Bui et al., 2011). The average discharge of the Red River at the Hanoi station (indicated by a triangle in Fig. 1) is 1160 m³/s during the dry season and 3970 m³/s during the rainy season (IMHE-MONRE, 2011). In the Red River, high concentration of suspended solids is always present that actually give it its “reddish” color. The tidal range along the coast is approximately 4 m. 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).

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 our previous studies (Bui et al., 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. Fig. 2 shows two out of the five cross-sections along the A-A' and B-B' lines shown in Fig. 1. The groundwater mostly exists as porous water that forms the topmost HUA and the shallow PCA, sandwiching the Holocene–Pleistocene aquitard. This aquitard however is completely missing in some places, thus creating hydrogeological windows that directly connect the two aquifer systems. 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 m²/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 80 m, and gradually increases from the northwest to southeast of the delta. The transmissivity ranges from 700 to 3000 m²/day and indicates a very high potential of groundwater resources. 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

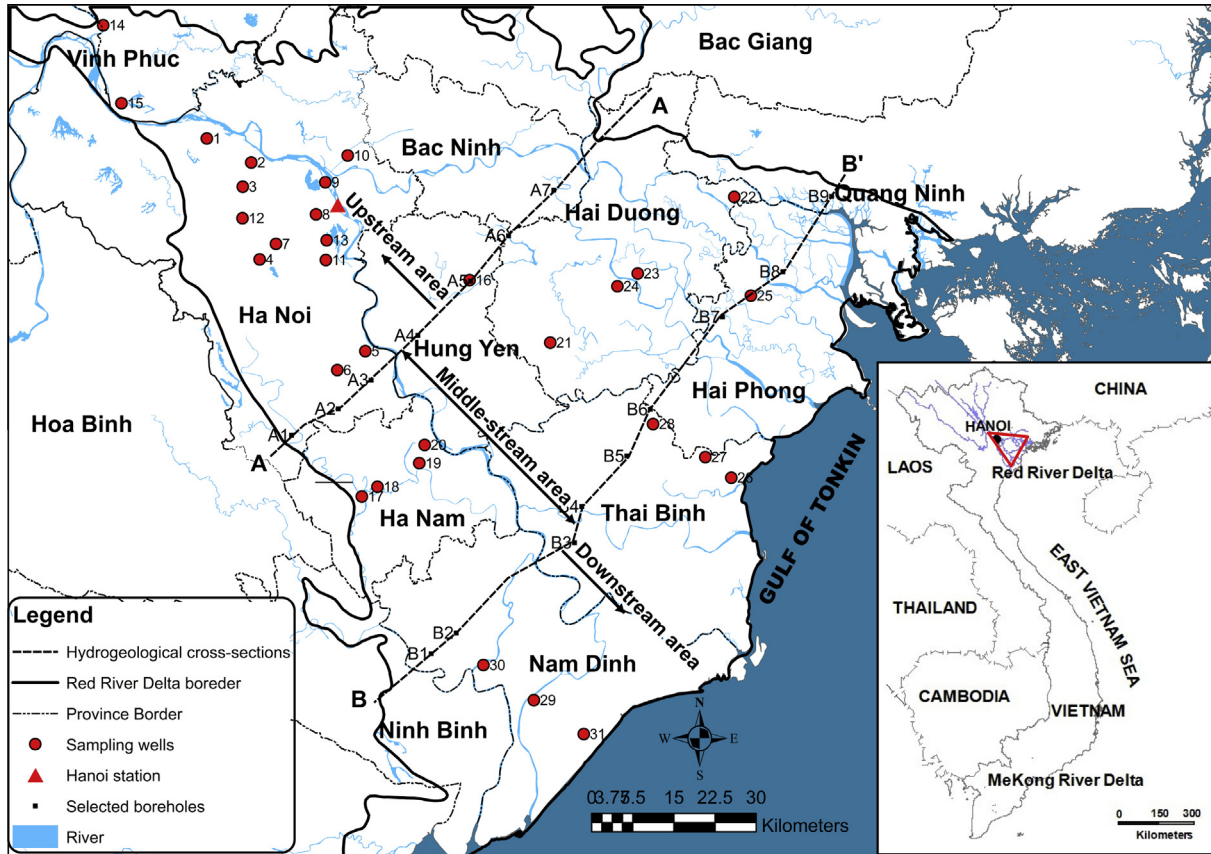


Fig. 1. Study area and location of sampling points.

predominantly recharged mainly by the surrounding mountain range and the vertical percolation of water coming from HUA through hydrogeological windows.

3. Data used and methods

3.1. Data used

Hydrogeochemical evaluation of groundwater systems is usually carried out with the availability of a large amount of groundwater chemical data (Hussein, 2004). 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. Details about this project and database were described in the project report (Tong, 2004).

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. To take

advantage of the data from the National Hydrogeological Database Project, we used the most recent groundwater chemical data, which were collected from 31 conjunctive observation wells for HUA and PCA 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^+ , 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). Standard quality control methods of the data used were applied to ensure accuracy in both sampling and laboratory procedures, and described in the following section (Section 3.2). Few samples were excluded from reporting for failing the accuracy criteria.

3.2. Methods

Groundwater samples were collected throughout the delta 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

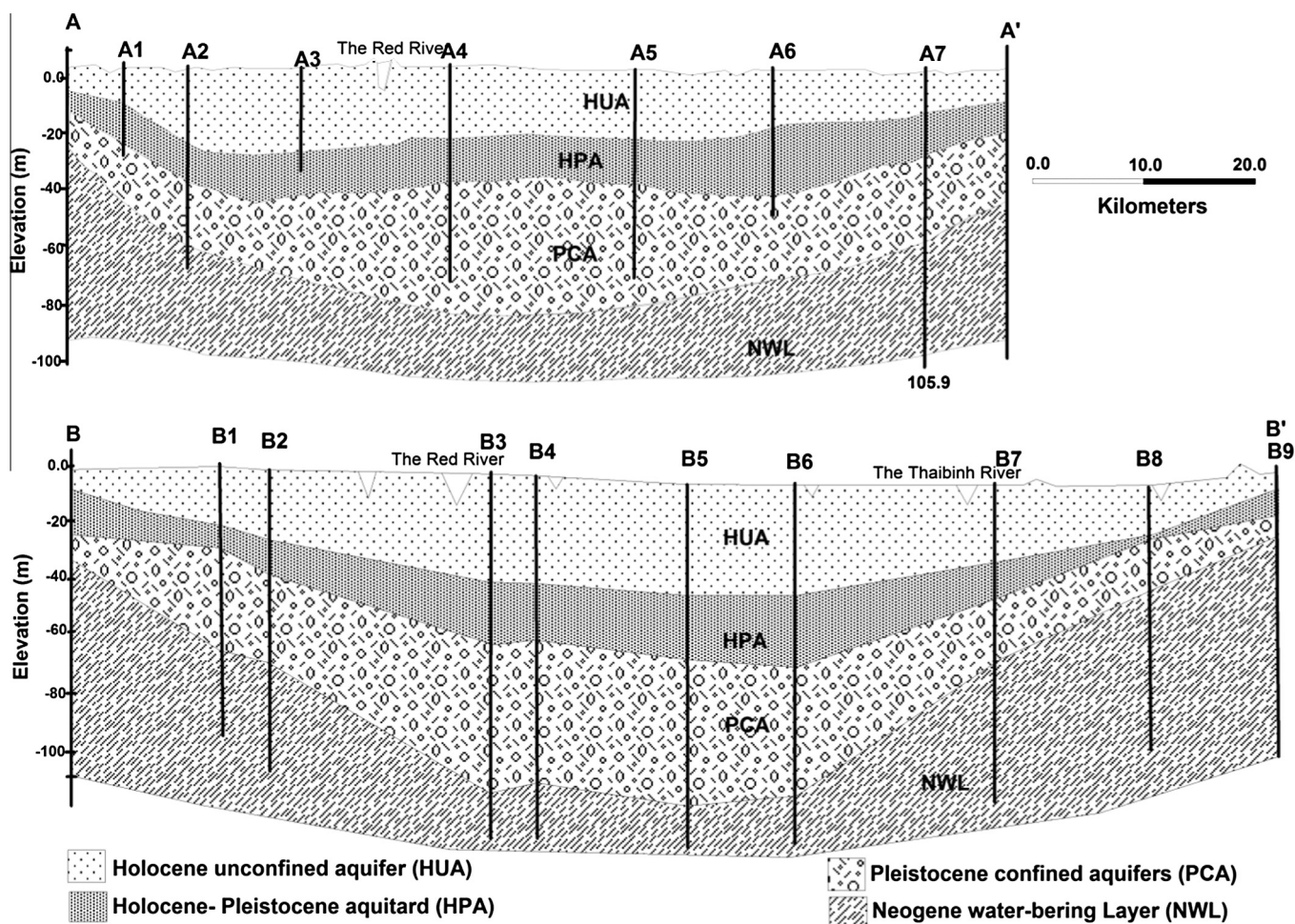


Fig. 2. Hydrogeological cross-sections along A-A', B-B' lines as shown in Fig. 1 (from Bui et al., 2011).

water quality of MONRE (2008). Major cation concentrations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) were analyzed by the atomic absorption spectrometry method. 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 analyses. The concentrations of Cl^- , HCO_3^- , and SO_4^{2-} anions were determined using Silver nitrate titration with chromate indicator (Mohr's method), ion chromatography method, and gravimetric method using barium chloride, respectively. The analytical precision for measurement of ions was determined by calculating the ionic balance error, which was within 5%.

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 $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, and $[\text{Na}^+]$ types. The right ternary diagram is divided into three anionic classification regions, the $[\text{HCO}_3^-]$, $[\text{Cl}^-]$, and $[\text{SO}_4^{2-}]$ 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.

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 $\text{Na}/(\text{Na} + \text{Ca})$ and $\text{Cl}/(\text{Cl} + \text{HCO}_3)$ 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). In the RRD, there are two main aquifers: HUA and PCA with the latter serving as the most important aquifer for the water supply. Therefore, this study also used the Gibbs diagram in order to investigate the factors governing groundwater chemistry not only in the unconfined aquifer, but also in the confined aquifer of the RRD.

4. Results

The statistical ranges and means of the monitored hydrogeochemical parameters in HUA and PCA, and their comparison with the Vietnamese and WHO drinking water standards are listed in Tables 1 and 2, respectively. Fig. 3 shows the Piper diagram plot for HUA. The numerical symbols in the figure correspond to the locations of the observation wells in Fig. 1. The non-bold and bold symbols correspond to the dry and rainy seasons, respectively. The Piper diagram for PCA was also created as shown in Fig. 4 to

examine the differences in the hydrogeochemical facies between HUA and PCA. To have a better view of the special distribution of water types identified by Piper diagrams (Figs. 3 and 4) in the RRD, Figs. 5 and 6 were created for HUA and PCA, 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 $[\text{Ca}^{2+}\text{--HCO}_3^-]$, $[\text{Na}^+\text{--HCO}_3^-]$, $[\text{Na}^+\text{--Cl}^-]$, $[\text{Mg}^{2+}\text{--HCO}_3^-]$, $[\text{Mg}^{2+}\text{--SO}_4^{2-}]$, $[\text{Mg}^{2+}\text{--Cl}^-]$, $[\text{Na}^+\text{--SO}_4^{2-}]$ and $[\text{Ca}^{2+}\text{--Cl}^-]$ types, respectively. The hydrogeochemical facies of all observation wells in Figs. 3 and 4 are summarized and tabulated in Table 3 to examine the differences between the two aquifers. In this table the differences between the two aquifers are expressed by bold letters and seasonal changes in the hydrogeochemical facies are indicated by hatched cells.

Fig. 7 shows the Gibbs diagram for groundwater in HUA. 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. 7a) and boundary G^- in the Gibbs anion diagram (Fig. 7b). 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. 7. The boundaries between these domains, however, were not clearly defined. According to Kumar et al. (2009), for groundwater, the domain of rock dominance extends further toward higher weight ratios as shown by the elongated boundaries, which in this study are presented by the boundaries as K^+ (Fig. 6a) and K^- (Fig. 7b), 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 and

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

Chemical parameter	WHO drinking standard value (maximum limit)	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	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)	500	250	0–946.19	59.1	3, 16	0–685.58	42.96	3, 16
Cl^- (mg/L)	250	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)	50 mg/L total nitrogen	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 2
Range of chemical parameters in PCA and their comparison with the Vietnamese and WHO standards for drinking water.

Chemical parameter	WHO drinking standard value (maximum limit)	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	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)	500	250	0–456.3	30.4	16	0–195.35	16.53	none
Cl^- (mg/L)	250	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)	50 mg/L total nitrogen	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

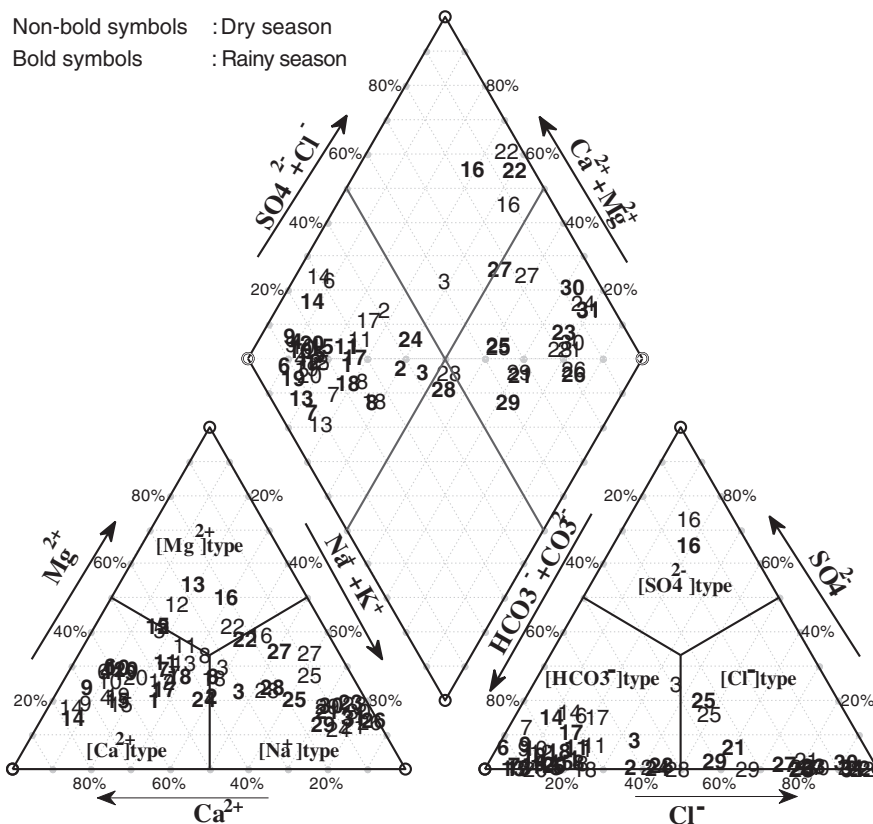


Fig. 3. Piper diagram for HUA groundwater in the Red River Delta.

4, the number symbols in Fig. 7 correspond to the locations of the observation wells in Fig. 1. The non-bold and bold symbols indicate the dry and rainy season data, respectively. To determine the source of the dissolved chemical components in the PCA groundwater, the Gibbs diagram was also created as shown in Fig. 8.

5. Discussions

5.1. Chemical quality of groundwater

Using the Tables 1 and 2, the suitability of groundwater in the RRD for drinking and domestic use was evaluated. By comparing Tables 1 and 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 et al., 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 1 and 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 in Tables 1 and 2 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. 16–24) and downstream areas of the delta (from Well Nos. 25–31) 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 1 and 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.

5.2. Hydrogeochemical facies and water types

Based on the left ternary diagram of Piper diagram plotted for HUA (Fig. 3), 31 and 26 out of the 62 groundwater samples (for

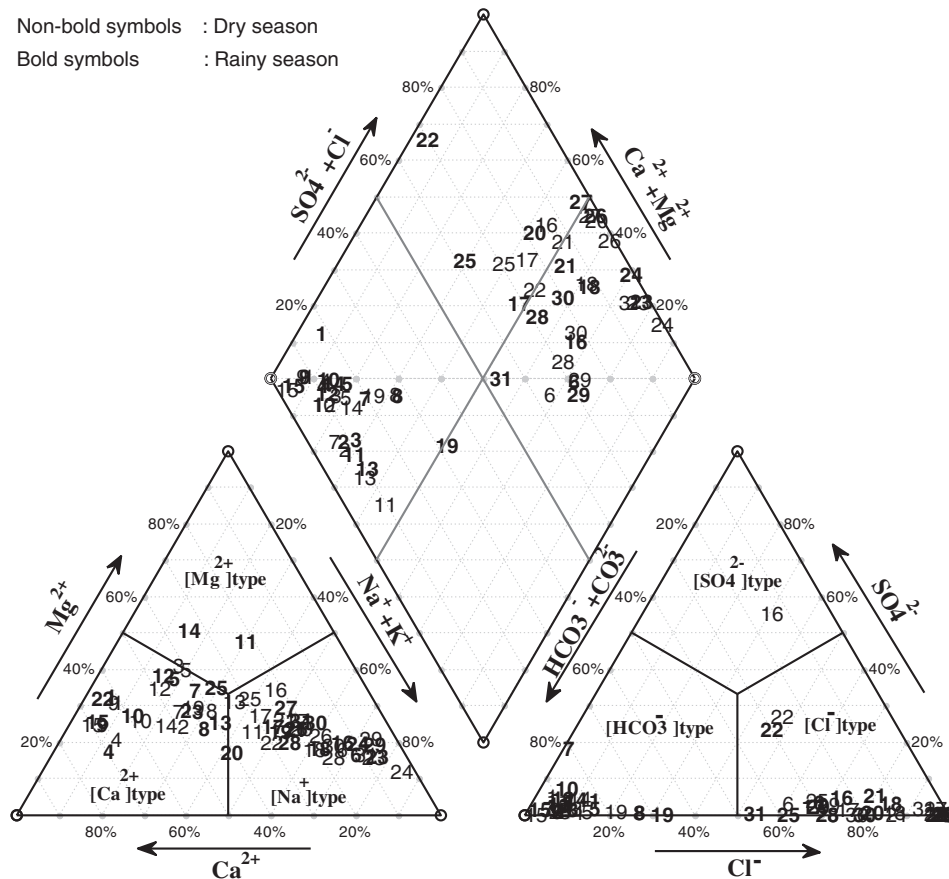


Fig. 4. Piper diagram for PCA groundwater in the Red River Delta.

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 in Fig. 3, 41 and 19 out of the 62 groundwater samples were $[HCO_3^-]$ and $[Cl^-]$ types, respectively, while 2 samples are of $[SO_4^{2-}]$ type. From the left ternary diagram of Piper diagram for PCA (Fig. 4), 24 and 33 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 of Fig. 4 on the other hand shows 30 and 31 samples to be of the $[HCO_3^-]$ and $[Cl^-]$ types, respectively, while only 1 sample is shown to be of the $[SO_4^{2-}]$ type.

Distribution of water types in HUA of the RRD (Fig. 5) shows that HUA has 6 water types during the dry season and 5 water types during the rainy season. PCA on the other hand, as shown in Fig. 6, has 5 and 6 water types during the dry and rainy seasons, respectively. In 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. 5. 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 predominance 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 pore-water 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.

In PCA (Fig. 6), similar to HUA, 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 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

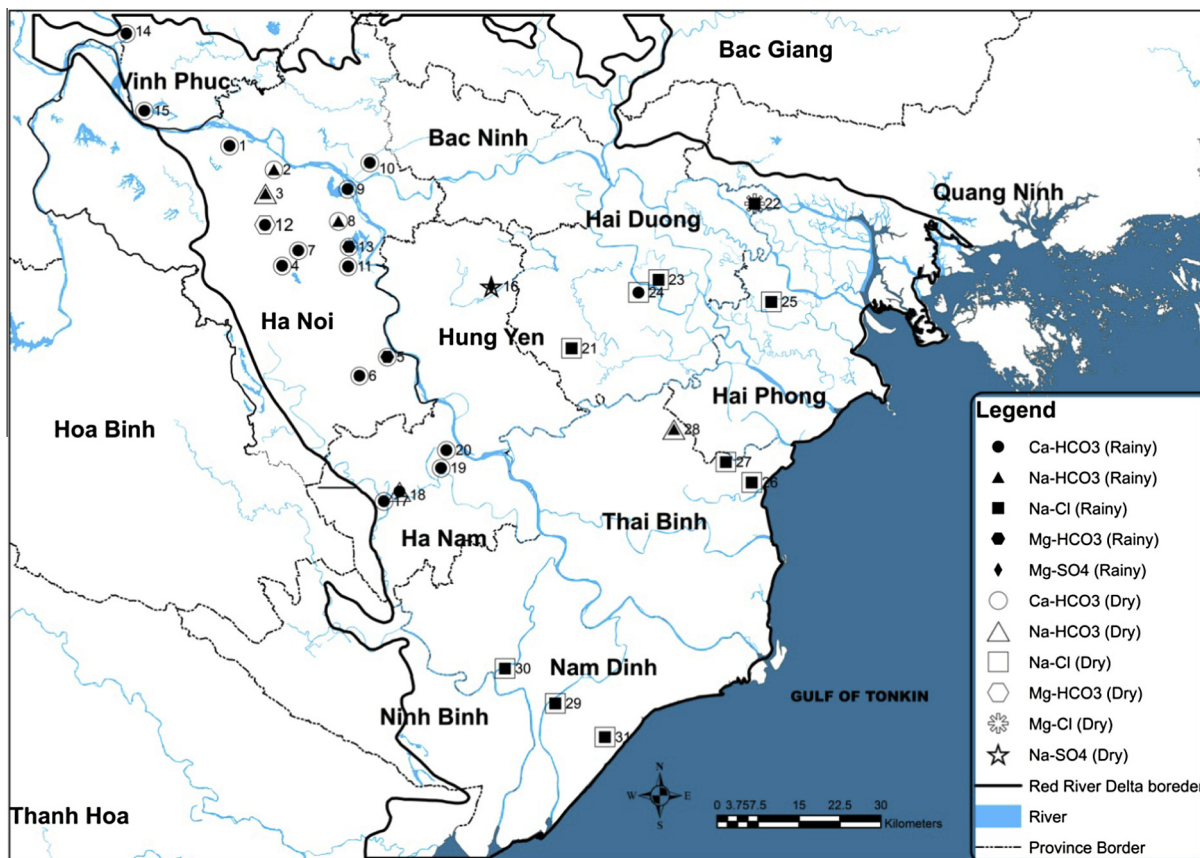


Fig. 5. Distribution of water type in HUA.

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.

Differences in the hydrogeochemical facies between HUA and PCA were observed by bold letters in Table 3. In total, 11 and 17 out of the 31 observation wells during the dry and rainy seasons, respectively 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 $[\text{Na}^+-\text{HCO}_3^-]$ type during the dry season, but concurrently of the $[\text{Mg}^{2+}-\text{HCO}_3^-]$ 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 $[\text{Ca}^{2+}-\text{HCO}_3^-]$ type, while PCA had the $[\text{Na}^+-\text{Cl}^-]$ type. In the middle-stream area, the water samples of HUA in Well Nos. 17, 18, 20 and 24 were of the $[\text{Ca}^{2+}-\text{HCO}_3^-]$ type during the rainy season, while PCA had the $[\text{Na}^+-\text{Cl}^-]$ 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 by hatched cells in Table 3. In 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 $[\text{Ca}^{2+}]$ to $[\text{Mg}^{2+}]$ type, and Well Nos. 2 and 8 changed from the $[\text{Ca}^{2+}]$ to $[\text{Na}^+]$ type. More interestingly, the water type in HUA Well No.24 changed in both cation and anion (from the $[\text{Na}^+-\text{Cl}^-]$ to $[\text{Ca}^{2+}-\text{HCO}_3^-]$ 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.

For PCA, there are 9 out of the 31 observation wells that show changes in the water type from the dry to the rainy seasons (Table 3). Similar to HUA, 8 out of the 9 wells showed changes in the cation type: from $[\text{Mg}^{2+}]$ to $[\text{Ca}^{2+}]$, from $[\text{Na}^+]$ to $[\text{Ca}^{2+}]$ or $[\text{Mg}^{2+}]$, or from $[\text{Ca}^{2+}]$ to $[\text{Mg}^{2+}]$ or $[\text{Na}^+]$. However, there is only one observation well (PCA Well No.16) that showed change in the anion type (from the $[\text{SO}_4^{2-}]$ to $[\text{Cl}^-]$ 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.

5.3. 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). As shown in Fig. 7, almost all HUA groundwater samples in both seasons from Well Nos. 1–15, which are located in the upstream area as shown in Fig. 1, 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. 17–20), 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

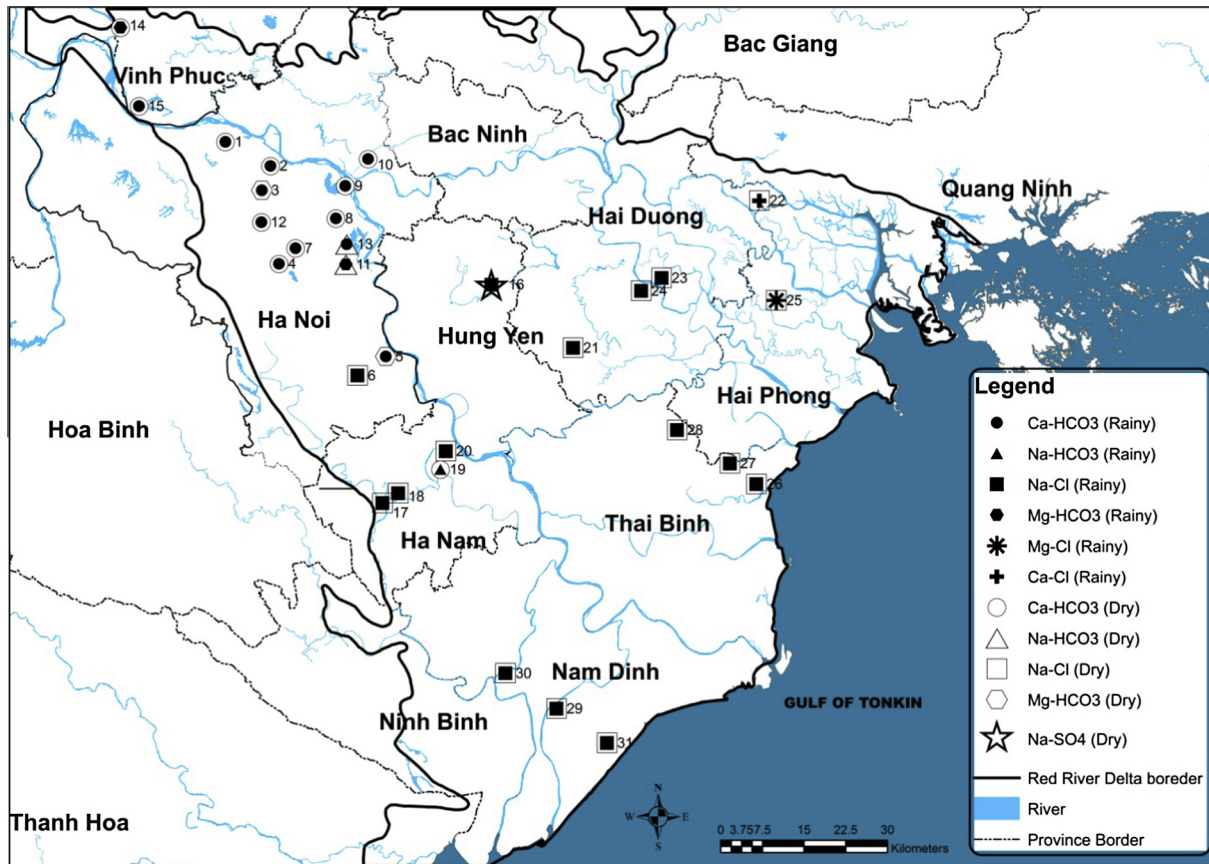


Fig. 6. Distribution of water type in PCA.

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. 25–31) fall outside the K^+ and K^- boundaries and toward the domain of evaporation dominance, except for HUA Well Nos. 25 and 28, which implies that marine activities such as salt water intrusion are 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 $Na/(Na + Ca)$, $Cl/(Cl + HCO_3)$. 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. 1), present remarkable decrease in TDS and in the weight ratio $Cl/(Cl + HCO_3)$. 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.

Similar to HUA, the Gibbs diagram for the PCA groundwater (Fig. 8) shows that almost all of samples (from Well Nos. 1–15) 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 $Cl/(Cl + HCO_3)$ (less than 0.1 as shown in Fig. 8b). This is consistent with the Piper diagram for PCA (Fig. 4), 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,

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. 8 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 $Cl/(Cl + HCO_3)$, 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 $Cl/(Cl + HCO_3)$ (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 $Cl/(Cl + HCO_3)$ 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

Table 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]

The bold letters represent the difference of water type between two aquifers, Holocene unconfined aquifer and Pleistocene confined aquifer.

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. 8). 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 Atalagbe, 2003), the Nile Delta in Egypt (Kashef, 1983), the Dibdibba Delta in Iraq (UN-ESCWA and BGR, 2013).

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. Like HUA, 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.

The differences in groundwater chemistry between HUA and PCA are also observed by comparing Figs. 7 and Fig. 8. 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 (Asia 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. 6 and 7) is that the HUA groundwater samples from Well Nos. 6 (southern of Hanoi), 17, 18 and 20 (Ha Nam province as shown in Fig. 1), 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

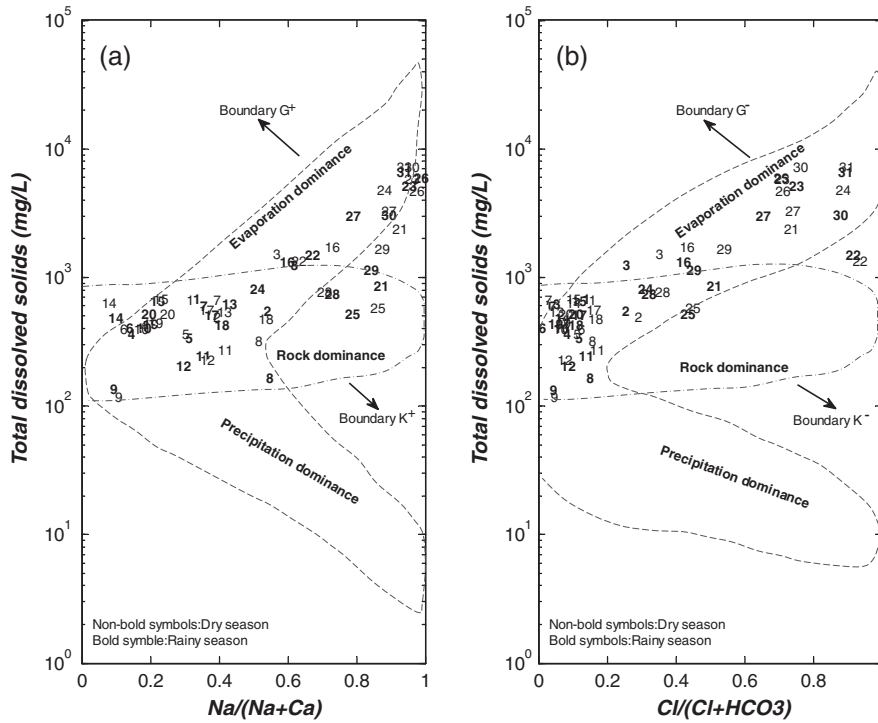


Fig. 7. Gibbs diagram for HUA groundwater in the Red River Delta.

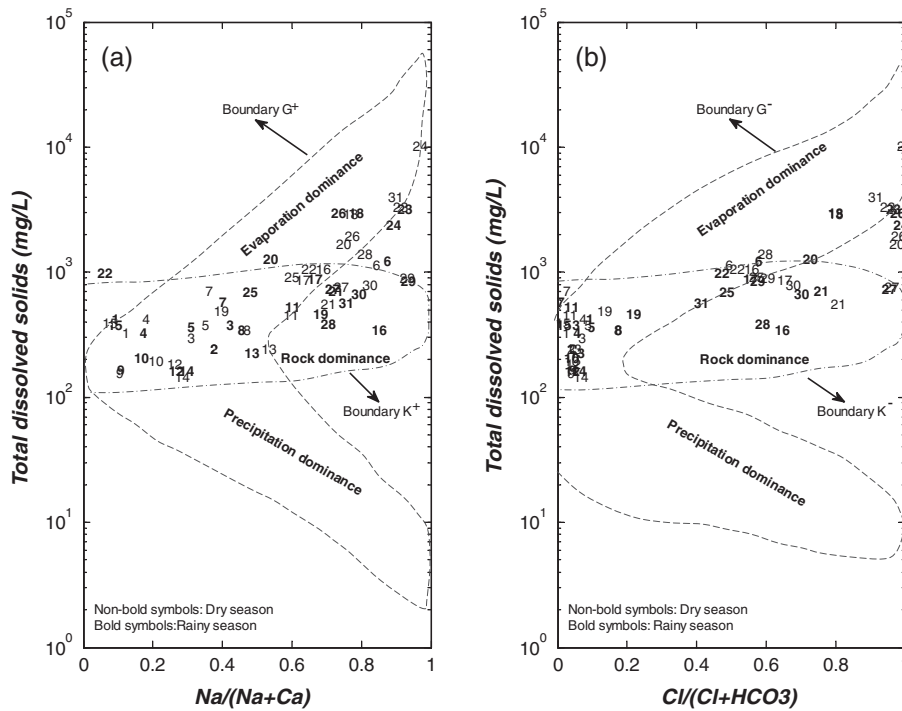


Fig. 8. Gibbs diagram for PCA groundwater in the Red River Delta.

sediments would be a source for high saline groundwater in deeper aquifers (PCA), whereas the HUA groundwater is affected by rainfall and surface water.

It is noted that the observation wells in the delta (Fig. 1) are denser in urbanized areas, and thus the results of spatio-seasonal hydrogeochemical properties for cities have higher accuracy than those for rural areas. The map showing spatial distribution of water

type (Figs. 7 and 8) would provide more insights if there were more observation wells in rural areas.

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 southwestern part of the 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 purposes. 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 Gibbs 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 Gibbs diagram. While the Piper diagram demonstrated the water types showing the essential chemical characters of different constituents in percentage values, the Gibbs diagram considers 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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