

Hydrogeochemical Characteristics of Groundwater in Hanoi, Vietnam

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Groundwater from the Holocene unconfined aquifer (HUA) and Pleistocene confined aquifer (PCA) is the major source of drinking and domestic water in Hanoi, Vietnam. A clear understanding of the groundwater hydrogeochemical properties, particularly their changes during dry and rainy seasons, is invaluable for the management and protection of this important water resource. In this study, the changes in the hydrogeochemical properties of groundwater during dry and rainy seasons were investigated by analyzing the major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^-) that were recently obtained in 2011 from 13 conjunctive sampling wells for HUA and PCA in Hanoi. The hydrogeochemical assessment was carried out using the Piper diagram and the Gibbs diagrams. Results from the Piper diagram indicated changes in the hydrogeochemical facies of at least 30% the sampling wells for both aquifers during the dry and rainy seasons. The changes were particularly pronounced in the cation-type facies, while the anion-type facies remained unchanged. Moreover, the hydrogeochemical facies of HUA was found to be different from that of PCA by approximately 50% for both dry and rainy seasons. In addition, the Gibbs diagrams showed apparent differences in the weight ratios $\text{Cl}/(\text{Cl}+\text{HCO}_3)$ between PCA and HUA. The results revealed that rock weathering is the main processes in the evolution of chemical composition of groundwater, but agricultural activities and salt water intrusion are the other important factors that affect groundwater chemistry in the study area.

Keywords: Hydrogeochemistry, Piper diagram, Gibbs diagrams, Holocene unconfined aquifer, Pleistocene confined aquifer, dry season, rainy season, Hanoi, Vietnam

1. Introduction

In almost all modern civilizations, groundwater is considered a vital water resource of drinking and domestic use. In Hanoi, the capital of Vietnam, nearly the entire population depends on groundwater for daily water consumption. Recently, the rapid urbanization and drastic increase in the population of Hanoi, as well as industrialization, have led to the unmitigated decline of groundwater levels (Bui et al., 2012) and the deterioration of water quality (Duong et al., 2003). Sustainable management of groundwater is thus necessary to secure its future availability and ecological value.

Hydrogeochemical facies, an important diagnostic chemical aspect of groundwater solutions occurring in hydrologic systems, is commonly examined in the assessment of groundwater quality. Hydrogeochemical facies analysis provides information on the distinct zones of cations and anions along different layers of aquifers (Christopher and Robert, 2005). Pollutants, such as heavy metals and organic compounds, generally interact with the ions present in groundwater. A clear view of the predominant ions can help understand the interaction and mechanisms of groundwater contamination.

The availability of a comprehensive groundwater database in Hanoi has attracted the interest of several researchers who wanted to investigate the effect of groundwater extraction and consumption suitability. Spatial and temporal analyses of groundwater levels show evidence of subsidence in several parts of Hanoi, which is generally attributed to overextraction (Bui et al., 2012). Furthermore, the analysis of water quality revealed that several groundwater sources are contaminated by arsenic (Berg et al., 2008). The cause and mode of contamination, however, are not clearly understood. The presence of deleterious substances in the aquifers of Hanoi is of immediate threat to the population. It is thus imperative to understand the hydrogeochemical processes for formulating appropriate

groundwater management plans. There is, however, little available information regarding the groundwater hydrogeochemical properties in Vietnam, including Hanoi.

Various researchers have carried out extensive hydrogeochemistry studies for assessing groundwater quality. 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. Baghvand et al. (2010) studied the groundwater quality of the Kashan Basin, central Iran, and characterized the groundwater species by using the Piper diagram. Arumugan and Elangovan (2009) assessed the groundwater quality of the Tirupur region in India for drinking and irrigation purposes by using the Piper diagram and sodium percentage values. However, there are few references regarding the changes in the hydrogeochemical properties during the dry and rainy seasons. This is perhaps because it is often assumed that the hydrogeochemical properties generally remain the same during the different seasons. Groundwater interacts with surface hydrologic systems, such as rivers, lakes, and oceans, and is indirectly influenced by seasonal changes during recharge and discharge. Thus, the change in seasons can potentially affect the hydrogeochemical properties of groundwater, especially in areas that have two distinct dry and rainy seasons, like Vietnam. Investigation of seasonal changes in the hydrogeochemical properties may reflect the groundwater hydrodynamics and circulation, which may help improve the data collection programs for groundwater assessment and enable better use of groundwater supplies. In addition, many researchers have focused on the hydrogeochemical properties of shallow (unconfined) aquifers with high probability to be contaminated by pollutants from domestic as well as agricultural and industrial sources (Marghade et al., 2012; Magesh et al., 2012). In Hanoi, groundwater from the Holocene unconfined aquifer (HUA) and Pleistocene confined aquifer (PCA) is the major source of water supply. High groundwater abstraction from PCA causes vertical percolation of water from HUA, leading to changes in groundwater chemistry. Therefore, the investigation of the different hydrogeochemical characteristics between the two aquifers, HUA and PCA, is critical for effective water management and water use planning.

In Hanoi, through an initiative of the national government (National Hydrogeological Database Project), groundwater quality data of the unconfined and confined aquifers were collected in 2011 during dry and rainy seasons. To take advantage of this unique and comprehensive database, this paper is the first attempt to investigate the hydrogeochemical characteristics of groundwater in HUA and PCA in Hanoi. Especially, this study aims to detect the changes in the hydrogeochemical properties during dry and rainy seasons. The Piper diagram and Gibbs diagrams were used to investigate the hydrogeochemical facies and to determine which factors govern groundwater composition not only in the unconfined aquifer but also in the confined aquifer. This study will provide valuable insights in understanding the changes during the dry and rainy seasons, as well as the differences between two aquifers in the groundwater hydrogeochemical properties in Hanoi.

2. Study area

Figure 1 shows the geographical locations of Hanoi and the 13 conjunctive sampling wells for both HUA and PCA used in this study. Hanoi is located at north-eastern Vietnam. It covers a total area of about 3400 km² and has a population of about 7 million (in 2011), which comprises approximately 7.5% of the total population of Vietnam. Hanoi is situated in the tropical monsoonal region with two distinct dry and rainy seasons. The rainy season starts in May and ends in October, while the dry season lasts from November until April. The annual average rainfall is about 1,600 mm, but in 2011, it was measured at 1,795 mm. The annual average humidity is about 80% and the average temperature is around 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. More than 100 lakes can be found in Hanoi, with a total surface

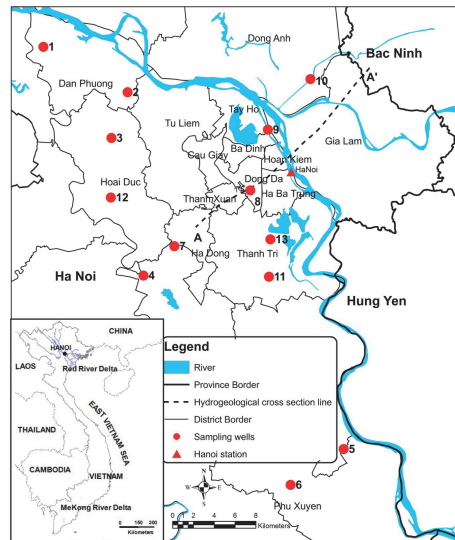


Fig. 1 Study area and distribution of sampling wells

area of more than 21.8 km². In 2011, the recorded average discharge of the Red River at the Hanoi station, shown by the triangle in Figure 1, was 2182 m³/s during the flood season and 927 m³/s during the dry season; both are lower than the average discharge in the past (3970 m³/s and 1160 m³/s, respectively). High concentration of suspended solids is always present in the Red River. The lakes, ponds and canals in Hanoi are highly polluted because of untreated domestic and industrial wastewater. Because groundwater is relatively cleaner and remains generally unaffected by the surface environmental problems, it has become the most trusted water source (Bui et al., 2011).

In terms of regional geology, Hanoi is underlain by the Pleistocene and Holocene sediments, with the latter being partly derived from postglacial marine transgressions and tectonic activity. According to our previous studies (Bui et al., 2011, 2012), there are two main aquifers, i.e. HUA and PCA, lying over the Neogene water-bearing Layer and sandwiching the Holocene-Pleistocene aquitard. This aquitard is however completely missing in some places, which create hydrogeological windows, as indicated in Figure 2, resulting in total connectivity between the two aquifer systems. HUA mainly consists of silty clay and various sands mixed with gravel. The thickness of this layer varies greatly up to more than 35m with an average of about 15 m. The transmissivity in HUA is from 20 to 1,788 m²/day. PCA consists of sand mixed with cobbles and pebbles, and is situated lower in the stratigraphic sequence. The thickness of PCA fluctuates over a large range with an average of about 35m, and gradually increases from north to south. The transmissivity ranges from 700 to 2900 m²/day and indicates 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 predominantly recharged by the vertical percolation of water coming from HUA through hydrogeological windows.

3. Data used

Groundwater samples were collected from the two major aquifers (HUA and PCA) in Hanoi using 13 conjunctive observation wells for HUA and PCA (Figure 1). The samples were collected in February (dry season) and August (rainy season) of 2011 and were analyzed according to ISO standard test methods for the following physico-chemical parameters: TDS, pH, major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺), major anions (HCO₃⁻, Cl⁻ and SO₄²⁻), NH₄⁺, NO₂⁻, and NO₃⁻. The carbonate ion (CO₃²⁻) was calculated from the observed bicarbonate (HCO₃⁻) and pH data (James 1982).

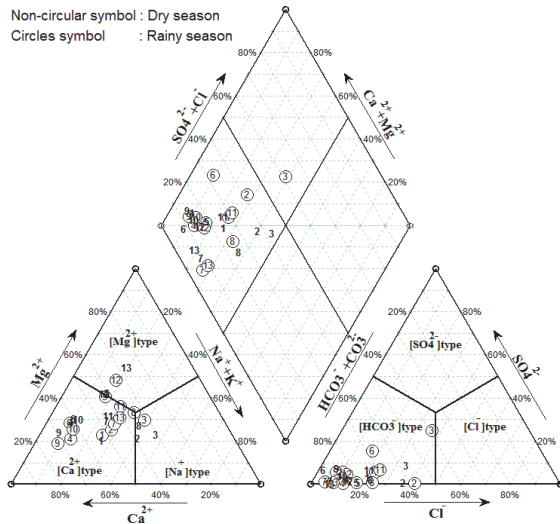


Fig. 2 Piper diagram for HUA GW

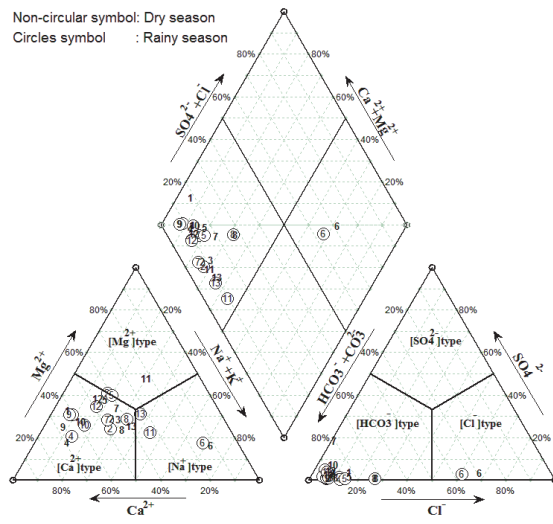


Fig. 3 Piper diagram for PCA GW

4. Results and Discussion

Hydrogeochemical facies and water types

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 physico-chemical parameter are plotted on a Piper diagram (Piper, 1944). 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 [Ca²⁺], [Mg²⁺], and [Na⁺] types, whereas the right ternary diagram is divided into three anionic classification regions, namely the [HCO₃⁻], [Cl⁻], and [SO₄²⁻] types. Each observation has a dominant cation and anion type. The combination of these predominant ion types is the hydrogeochemical facies of the aquifer at a specific observation well. After plotting the data, the hydrogeochemical facies of each well was investigated for changes related to the dry and rainy seasons by comparing the dominant ions.

Figure 2 shows the Piper diagram plot for HUA. The number symbols in this figure correspond to the locations of the observation wells in Figure 1. The non-circular symbols and circles indicate the dry and rainy seasons, respectively. As indicated in the left ternary diagram of Figure 2, the water samples identified as the [Ca²⁺], [Na⁺], and [Mg²⁺] types are 19, 4 and 3, respectively. The right ternary diagram shows all water samples to be of the [HCO₃⁻] type. Thus, HUA is mostly of the [Ca²⁺-HCO₃⁻] type (calcium ion-bicarbonate ion type). To examine the differences in the hydrogeochemical facies between HUA and PCA, the Piper diagram for PCA was also created as shown in Figure 3. From the left ternary diagram, the numbers of the [Ca²⁺], [Na⁺], and [Mg²⁺] types are 19, 4 and 3, respectively. The right ternary diagram indicates that 24 out of the 26 samples are dominated by the [HCO₃⁻] type, while the remaining two samples (both in well P6) are of the [Cl⁻] type. Thus, like HUA, the groundwater in PCA is primarily of the [Ca²⁺-HCO₃⁻] type. Changes in the hydrogeochemical facies during the dry and rainy seasons are observed in both HUA and PCA. For instance, in well H13 of HUA, the water type during the dry season was [Ca²⁺-HCO₃⁻], but became [Mg²⁺-HCO₃⁻] during the rainy season. In P11 of PCA, it was of the [Na⁺-HCO₃⁻] type during the dry season and changed to the [Mg²⁺-HCO₃⁻] type during the rainy season.

To have a better view of these changes, the hydrogeochemical facies of all observation wells in Figures 2 and 3 are summarized and tabulated as shown in Table 3. In HUA, the hydrogeochemical facies of 5 out of the 13 observation wells exhibited seasonal changes, particularly of the cation type. H5 and H13 changed from the [Ca²⁺] to [Mg²⁺] type and H12

Table 1 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 ⁻]

changed from the [Mg²⁺] to [Ca²⁺] type. This may be due to recharge from surface water such as rainfall, lake, or river. H2 and H8 changed from the [Ca²⁺] to [Na⁺] type, which suggests the influence from surface water to groundwater in HUA during the rainy season. Regarding PCA, 4 out of the 13 observation wells showed changes in the cation type during the dry and rainy seasons. P3 and P5 changed from the [Mg²⁺] to [Ca²⁺] type, P11 changed from the [Na⁺] to [Mg²⁺] type, and P13 changed from the [Na⁺] to [Ca²⁺] type. This implies that water infiltration from HUA may affect the concentrations of chemical constituents of the PCA groundwater during the rainy season through hydrogeological windows, as mentioned above.

It is worth to note that the differences in the hydrogeochemical facies between the two aquifers are also observed in Table 3. For instance, the water in H3 of HUA was of [Na⁺-HCO₃⁻] type during the dry season, but concurrently of the [Mg²⁺-HCO₃⁻] type in P3 of PCA. Interestingly, during the rainy season, the water in H2 of HUA was of the [Na⁺-HCO₃⁻] type, but of the [Ca²⁺-HCO₃⁻] type in P2 of PCA. In total, 6 out of the 13 observation wells during the dry season and 7 out of the 13 during the rainy season exhibited differences in the water type between the two aquifers. These differences are possibly influenced by the materials in the two aquifers, as well as interaction with surface water and between the two aquifers, which affect the groundwater chemical characteristics and flow paths.

Factors governing water chemistry

A chemical diagram of the major natural mechanisms controlling the composition of the dissolved solids in surface water was proposed by Gibbs (1970). The weight ratios Na/(Na+Ca) and Cl/(Cl+HCO₃) against the total dissolved solids (TDS) on a logarithmic axis were plotted separately in two diagrams, a Gibbs cation diagram and a Gibbs anion diagram. Although the Gibbs diagrams were originally applied to surface water, they are widely used to assess the functional sources of dissolved chemical constituents in groundwater in shallow (unconfined) aquifers, which have high potential for being influenced by surface water (Marghade et al. 2012, Raju et al. 2011, Nagarajan et al. 2010). This study is the first attempt to use the Gibbs diagrams as reference for assessing the factors governing groundwater chemistry in a confined aquifer as well as an unconfined aquifer in the study area.

Figure 4 shows the Gibbs diagrams for groundwater in HUA. Gibbs (1970) found that the

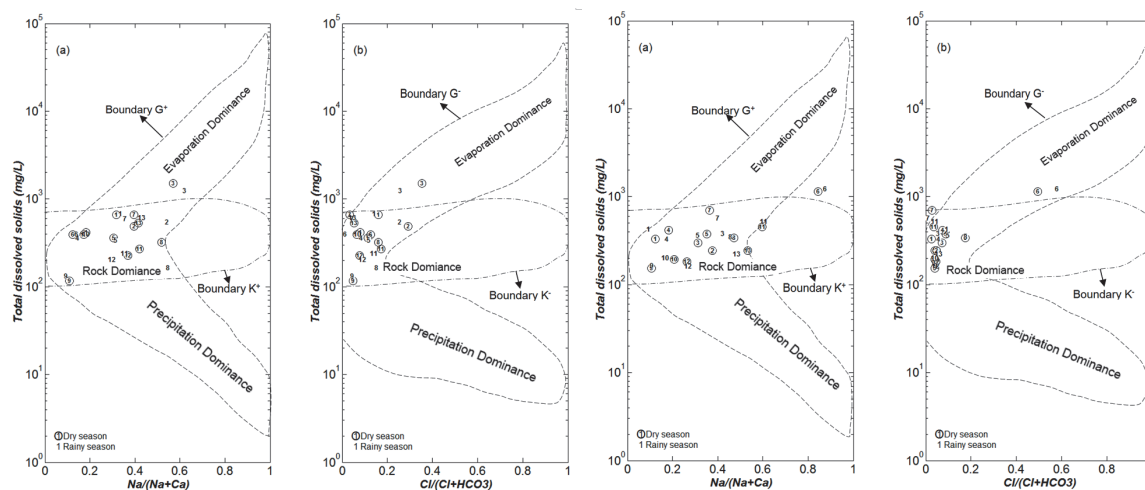


Fig.5 Gibbs diagram for HUA GW

Fig.6 Gibbs diagrams for PCA GW

composition of most of the world's surface water falls in the boundaries, which the authors expressed in this study as boundary G^+ on the Gibbs cation diagram (Figure 4a) and boundary G^- on the Gibbs anion diagram (Figure 4b). The area inside these boundaries was subdivided into three domains (precipitation dominance, rock dominance, and evaporation dominance) by Gibbs (1970) on the basis of analytical chemistry data, which represent the three major natural mechanisms controlling surface water chemistry as indicated in Figure 4. In order to make these domains clear, Kumar (2009) delineated the boundaries of the rock-water interaction dominance field, which were also adopted by other researchers (Ravikumar et.al, 2011, Raju et.al, 2011). For clarity in this study, these boundaries are presented by the boundaries K^+ on the Gibbs cation diagram (Figure 4a) and K^- on the Gibbs anion diagram (Figure 4b). As in the Piper diagram, the number symbols in the figures correspond to the locations of the observation wells in Figure 1. The non-circular symbols and circles indicate dry and rainy season data, respectively.

As shown in Figure 4, 12 out of the 13 groundwater wells fall inside not only G^+ , G^- but also K^+ , K^- boundaries, which suggests that rock-water interaction is the major source for dissolved ions in HUA. In general, there are no significant changes in the weight ratios $Na/(Na+Ca)$ and $Cl/(Cl+HCO_3)$ between the dry and rainy seasons as well as TDS in HUA. Note that two groundwater samples from well H3 show the highest TDS and high weight ratios $Na/(Na+Ca)$ and $Cl/(Cl+HCO_3)$ among the HUA wells for both seasons, and thus fall outside the K^+ and K^- boundaries. With closer inspection of land use, this well is located in an agricultural area of intensive irrigation (Nguyen, 2010). Therefore, it is reasonable to infer that agricultural activities cause the groundwater samples of H3 to fall outside the domain of rock dominance.

To determine the functional source of the dissolved chemical components in the PCA groundwater, the Gibbs diagrams were also created as shown in Figure 5. This figure indicates that there are no significant differences between the dry and rainy seasons for the groundwater samples in PCA, which is similar to the result in HUA. However, from Figures 4b and 5b, it is interesting to note that the weight ratios $Cl/(Cl+HCO_3)$ of the PCA groundwater samples are obviously different from those in HUA. The ratios in the PCA samples are extremely low, less than 0.1 in 11 out of the 13 sampling wells, whereas the same ratios in the HUA samples reach values up to 0.4. This is consistent with the Piper diagram for PCA (Figure 3), where the $[HCO_3^-]$ type is exceedingly dominant in the PCA groundwater (except for sampling well P6 as explained later). This observation implies that the PCA groundwater chemistry is controlled by the dissolution of carbonate minerals, whereas the HUA groundwater composition is

affected by the dissolution of carbonate minerals and surface water. Figure 5 also shows that the PCA groundwater samples were plotted mostly inside the G^+ , G^- , K^+ , and K^- boundaries. This suggests that rock-water interaction is the main factor controlling the chemical composition of the PCA groundwater. However, two groundwater samples from well P6 clearly deviate from the others by falling outside the boundaries G^+ and K^+ in Figure 5a and outside boundary K^- but inside G^- in Figure 5b. On the other hand, the Piper diagram for PCA (Figure 3) shows that the $[Na^+]$ and $[Cl^-]$ types dominated in this sampling well in both seasons. Another noteworthy point emerging from the Gibbs diagrams for HUA (Figure 4) is that the HUA groundwater samples at the same location (well H6) have low weight ratios $Na/(Na+Ca)$ and $Cl/(Cl+HCO_3)$. Presumably, in the area of the P6 well, salt water intrusion affects the deeper aquifer (PCA), whereas the HUA groundwater is affected by rainfall and surface water.

4. Conclusion

The main objectives of this study are to investigate the changes during dry and rain seasons in hydrogeochemical facies and to determine factors governing water chemistry of groundwater not only HUA but also in PCA. In this paper, taking advantage of the unique database, hydrogeochemical parameters from 13 conjunctive sampling wells for HUA and PCA in Hanoi acquired during dry and rainy season in 2011 were comprehensively analyzed.

In terms of hydrogeochemical facies, from analysis of the Piper diagrams for HUA and PCA, the following generalizations were obtained as the groundwater properties in Hanoi: the $[Ca^{2+}]$ type groundwater is quite abundant in both aquifers; almost all groundwater in the 13 conjunctive observation wells is of the $[HCO_3^-]$ type during the dry and rainy seasons in both aquifers. A change in the hydrogeochemical facies was detected from the dry to the rainy season in at least 30% 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 unchanged. Differences in the hydrogeochemical facies between HUA and PCA were also observed in the majority of the observation wells (6 out of the 13 observation wells during the dry season and 7 out of 13 during the rainy season).

The Gibbs diagrams suggest that rock dissolution is apparently the dominant process affecting the groundwater composition in both aquifers. The results from the Gibbs diagrams show no significant changes in the weight ratios $Na/(Na+Ca)$ and $Cl/(Cl+HCO_3)$ as well as the TDS of the groundwater samples in both seasons and both aquifers. The results also indicate that the PCA weight ratios $Cl/(Cl+HCO_3)$ are obviously different those in HUA. The weight ratios $Cl/(Cl+HCO_3)$ are extremely low in PCA, less than 0.1 in most of the samples, whereas in the HUA samples, they were scattered within the zone of rock dominance. Furthermore, it is reasonable to argue that agricultural activities and salt water intrusion are the additional factors that cause some samples to fall outside the zone of rock dominance. The findings of this study provide valuable information regarding the groundwater hydrogeochemical properties and hydrodynamics in Hanoi, Vietnam.

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