

## **Decadal Change in the Hydrogeochemical Facies of Groundwater during Dry and Rainy Seasons in Hanoi, Vietnam**

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### **Abstract**

In Hanoi, the capital of Vietnam, nearly the entire population depends on groundwater for daily water consumption because of the uneven distribution and contaminated quality of surface water resources. In recent years, the drastic increase in the population of Hanoi has severely created greater demand for this valuable water resource, leading to the unmitigated decline of groundwater levels and the deterioration of water quality. A clear understanding of its hydrogeochemical properties, particularly the decadal changes, will be of invaluable use in managing and protecting this very important water resource. In this study, the decadal change in the hydrogeochemical characteristics of groundwater from the Pleistocene confined aquifer (PCA) was investigated by analyzing the major ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ). These hydrogeochemical data were obtained from the physiochemical analysis of water samples from 15 PCA wells in Hanoi, taken in 1993, 2003 and 2011. The hydrogeochemical assessment was carried out using the Piper diagram and the Gibbs diagrams. Results from the Piper diagram indicated the decadal changes in the hydrogeochemical facies of at least 30% the sampling wells for dry and rainy seasons. The changes were particularly pronounced in the cation-type facies, while the anion-type facies remained almost unchanged. Moreover, the results also show that there are more groundwater samples showing the changes in the hydrogeochemical facies during the period of 2003 – 2011 than during the period of 1993-2003. Although the Gibbs diagrams suggested that rock weathering is the main processes in the evolution of chemical composition of groundwater, contemporary anthropogenic activities, such as irrigation, industrialization and urbanization perhaps affect

groundwater chemistry in the study area, leading to the decadal changes of hydrogeochemical facies.

**Keywords:** hydrogeochemical facies, Piper diagram, Gibbs diagrams, Pleistocene confined aquifer, Hanoi, Vietnam.

## **1. Introduction**

In Hanoi, the capital of Vietnam, nearly the entire population depends on groundwater for daily water consumption because of the uneven distribution and poor quality of surface water resources. Recently, the combination of rapid population growth, urbanization and industrialization results in overexploitation of the groundwater resources in the region. The continuous high water demand leads to the unmitigated decline of groundwater levels [1] and the deterioration of water quality [2]. Sustainable management of groundwater is thus necessary to secure its future availability and ecological value.

There have been quite a few studies on the groundwater in Hanoi reported in literature. Nguyen and Helm [4], for example, investigated on land subsidence due to excessive groundwater exploitation. Spatial and temporal analyses of groundwater levels in Hanoi were carried out by Bui et al [4]. Duong et al. [2] considered groundwater quality, pollution and monitoring system design. Groundwater arsenic contamination was identified in some parts of Hanoi [5]. However, there is little available information regarding the groundwater hydrogeochemical properties (such as hydrogeochemical facies), which could provide fundamental references for further groundwater analyses ensuring sustainable groundwater development in Vietnam, including Hanoi.

The chemical composition of groundwater is controlled by many factors including the mineralogy of aquifers, the composition of precipitation and surface water, climate, topography, and anthropogenic activities [6]. The interaction of groundwater with these factors leads to the formation of different hydrogeochemical facies [7]. Therefore, hydrogeochemical facies is one of the most effective tools used to differentiate various forms of geochemical reaction and to infer environmental factors affecting groundwater quality and its flow. This can help understand the geochemical processes, hydrodynamics, origin and interaction of groundwater with aquifer materials.

Various researchers have carried out extensive hydrochemistry studies for assessing groundwater quality. For example, Marghade et al. [8] assessed the

chemistry of major ions of shallow groundwater to understand the groundwater geochemical evolution and water quality in Nagpur city, central India. Baghvand et al. [9] studied the groundwater quality of the Kashan Basin, central Iran and characterized the groundwater species by using the Piper diagram. However, very few studies have looked at the decadal changes in the hydrogeochemical properties. In fact, evaluation of temporal changes in hydrogeochemical facies is a difficult issue because groundwater chemistry data commonly have short record length, limited spatial coverage, and high uncertainty. On the other hand, 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 distinct dry and rainy seasons, like Vietnam. Therefore, the investigation of decadal changes as well as changes from the dry to rainy seasons 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.

Through implementing a National Hydrogeological Database Project under the support and nomination of the Ministry of Resources and Environment, Vietnam, we have constructed and maintained a costly groundwater monitoring database to gather all the observed groundwater data. To take advantages of our internally- available data sets, the main objective of this study was to investigate decadal changes in the groundwater hydrogeochemical properties in Hanoi and to deduce a hydrogeochemical evaluation of the aquifer system based on the ionic constituents, water types, and factors controlling groundwater quality. To achieve the expected goals, groundwater quality data of the confined aquifers in three years, 1993, 2003 and 2011 during dry and rainy seasons were collected and analyzed. The Piper diagram was used to investigate the hydrogeochemical facies. Decades of studies have already proven the efficacy and robustness of the Piper diagram method in classifying the ions in the groundwater into various hydrogeochemical types [9][10]. Gibbs [11] proposed chemical diagrams for assessing the functional source of dissolved chemical constituents and showed the mechanism controlling the chemistry of surface water. Various researchers have already demonstrated the usefulness of these diagrams for groundwater of shallow (unconfined) aquifers [12]. In this study, the Gibbs diagrams were used as

reference to determine which factors govern composition of groundwater in the confined aquifer. This study will provide valuable insights in understanding the decadal changes in the groundwater hydrogeochemical properties in Hanoi, especially under the looming effects of climate change.

## 2. Study Area

Fig.1 shows the geographical locations of Hanoi and the 15 sampling wells in the Pleistocene confined aquifer used in this study. Hanoi is located at north-eastern Vietnam. It covers a total area of about 3400 km<sup>2</sup> 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/km<sup>2</sup>. More than 100 lakes can be found in Hanoi, with a total surface area of more than 21.8 km<sup>2</sup>. In 2011, the recorded average discharge of the Red River at the Hanoi station, shown by the triangle in Fig.1, was 2182 m<sup>3</sup>/s during the flood season, and 927 m<sup>3</sup>/s during the dry season; both are lower than the average discharge in the past (3970 m<sup>3</sup>/s and 1160 m<sup>3</sup>/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

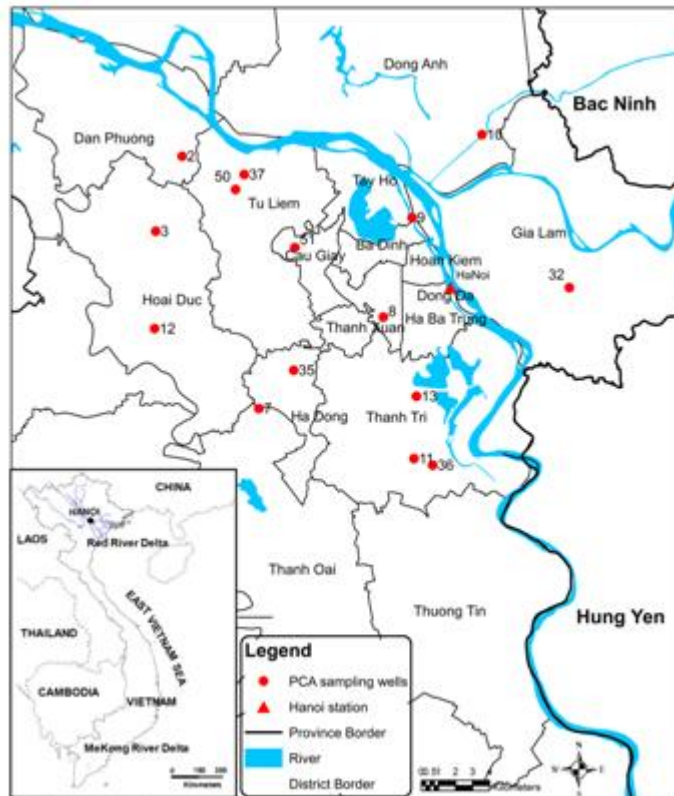


Figure 1. Study area and distribution of sampling wells

wastewater. Because groundwater is relatively cleaner, and remains generally unaffected by the surface environmental problems, it has become the most trusted water source [1].

### **3. Data used**

Groundwater samples were collected from the Pleistocene aquifer in Hanoi using observation wells (Fig.1). The samples were collected in February (dry season) and August (rainy season) of three years (1993, 2003 and 2011) and were analyzed according to ISO standard test methods [13] for the following physico-chemical parameters: TDS, pH, major cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ), major anions ( $\text{HCO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ),  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$ . The water analyses were conducted in the laboratories of the Ministry of Natural Resources and Environment. The carbonate ion ( $\text{CO}_3^{2-}$ ) was calculated from the observed bicarbonate ( $\text{HCO}_3^-$ ) and pH data [14].

## **4. Results and Discussion**

### **4.1. Hydrogeochemical Facies and Water types**

The term “hydrochemical facies” is used to describe the occurrence modes of groundwater in an aquifer with respect to chemical composition. To determine the hydrochemical facies of groundwater, the percentages of the equivalents of each physico-chemical parameter are plotted on a Piper diagram [15]. 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, whereas the right ternary diagram is divided into three anionic classification regions, namely the [ $\text{HCO}_3^-$ ], [ $\text{Cl}^-$ ], and [ $\text{SO}_4^{2-}$ ] types. Each observation has a dominant cation and anion type. The combination of these predominant ion types is the hydrochemical facies of the aquifer at a specific observation well. After plotting the data, the hydrochemical facies of each well was investigated for decadal changes by comparing the dominant ions. Figs 2, 3 and 4 show the Piper diagram plot for PCA groundwater in 1993, 2003 and 2011, respectively.

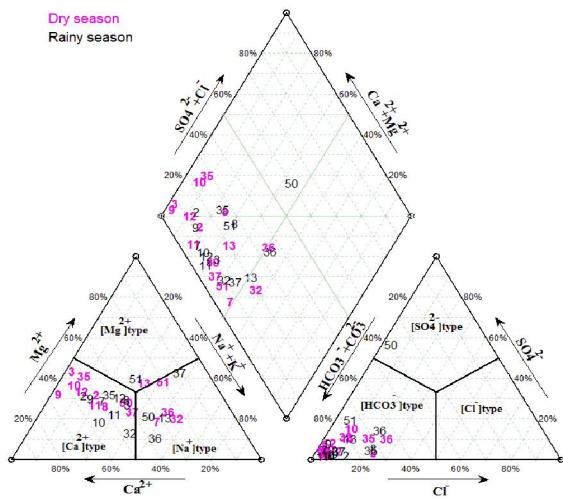


Figure 2. Piper diagram for groundwater in 1993

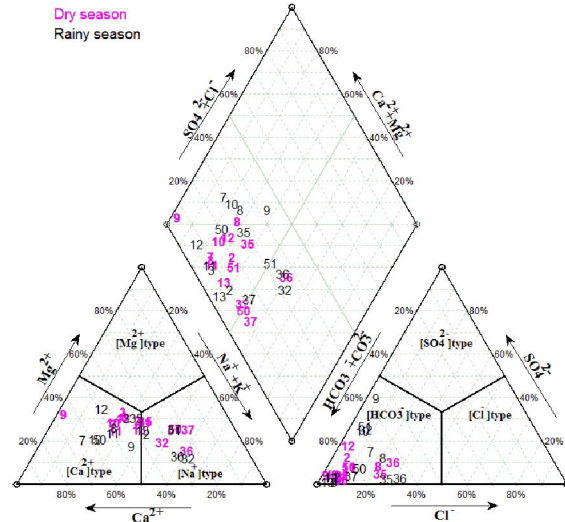


Figure 3. Piper diagram for groundwater in 2003

The numeric symbols and their color in these figures correspond to the locations of the observation wells in Fig.1 and the dry and rainy seasons. As indicated in the left ternary diagram of these figures, the water samples identified as the  $[Ca^{2+}]$ ,  $[Na^+]$ , and  $[Mg^{2+}]$  types are 27, 15 and 3 during dry season and 29, 13 and 3 during rainy season, respectively. The right ternary diagram shows all water samples during dry season and 44 out of 45 during rainy season are dominated by the  $[HCO_3^-]$  type. Thus, PCA is mostly of the  $[Ca^{2+}-HCO_3^-]$  type (calcium ion-bicarbonate ion type).

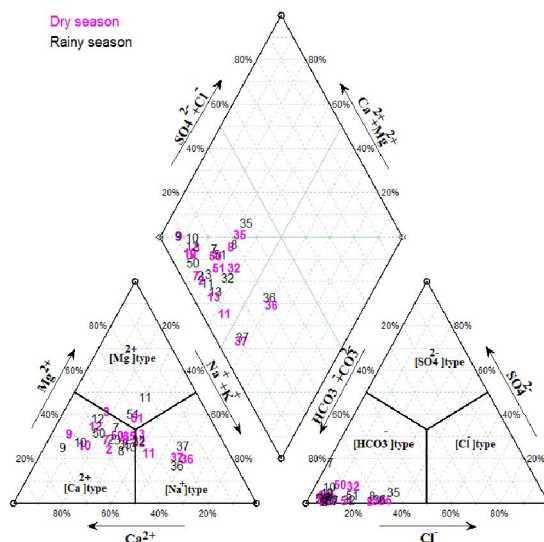


Figure 4. Piper diagram for groundwater in 2011

As shown in Fig.2, 5 out of the 15 samples exhibited changes in the cation type from the dry to rainy seasons such as from  $[Na^+]$  to  $[Ca^{2+}]$ , or from  $[Mg^{2+}]$  to  $[Ca^{2+}]$ , or from  $[Ca^{2+}]$  to  $[Na^+]$ . There is only one observation well No 61 showing

change in both cation and anion types (from  $[Ca^{2+} - HCO_3^-]$  to  $[Na^+ - SO_4^{2-}]$ ). Figs. 3 and 4 also show the changes in water type from the dry to the rainy season in 4 and 3 out of the 15 samples in 2003 and 2011, respectively. These changes imply that water infiltration from the upper aquifer (Holocene unconfined aquifer) may affect the concentrations of chemical constituents of the PCA groundwater through hydrogeological windows that directly connect the two aquifer systems.

To have a better view of the decade changes, the hydrogeochemical facies of all observation wells in Figs. 2, 3 and 4 are summarized and tabulated as shown in Table 1. As shown in table 1, 9 out of 30 dry and rainy samples show the changes in the hydrochemical facies during the periods of 1993-2003 whereas 10 out of 30 show the changes during the period of 2003-2011. This is perhaps due to the effect of contemporary anthropogenic activities such as irrigation, industrialization and urbanization on the chemical characteristics of the groundwater.

**Table 1** .Water types of groundwater samples in PCA

Sampling Well	1993		2003		2011	
	Dry	Rainy	Dry	Rainy	Dry	Rainy
2	Ca-HCO3	Ca-HCO3	Ca-HCO3	Na-HCO3	Ca-HCO3	Ca-HCO3
3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Mg-HCO3	Ca-HCO3
7	Na-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3
8	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3
9	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3
10	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3
11	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Na-HCO3	Mg-HCO3
12	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3
13	Mg-HCO3	Na-HCO3	Ca-HCO3	Na-HCO3	Na-HCO3	Ca-HCO3
32	Na-HCO3	Ca-HCO3	Na-HCO3	Na-HCO3	Na-HCO3	Na-HCO3
35	Ca-HCO3	Ca-HCO3	Na-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3
36	Na-HCO3	Na-HCO3	Na-HCO3	Na-HCO3	Na-HCO3	Na-HCO3
37	Ca-HCO3	Na-HCO3	Na-HCO3	Na-HCO3	Na-HCO3	Na-HCO3
50	Ca-HCO3	Na-SO4	Na-HCO3	Ca-HCO3	Ca-HCO3	Ca-HCO3
51	Na-HCO3	Mg-HCO3	Na-HCO3	Na-HCO3	Mg-HCO3	Mg-HCO3

#### 4.2. 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 [11]. The weight ratios  $Na/(Na+Ca)$  and  $Cl/(Cl+HCO_3)$  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 [12]. This study used the Gibbs diagrams as reference in order to assess the factors governing groundwater chemistry in PCA in the study area.

Fig. 5, 6 and 7 shows the Gibbs diagrams for PCA groundwater in 1993, 2003 and 2011. Gibbs [11] found that the 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 (Figs. 5a, 6a, 7a) and boundary  $G^-$  on the Gibbs anion diagram (Figs. 5b, 6b, 7b). The area inside these boundaries was subdivided into three domains (precipitation dominance, rock dominance, and evaporation dominance) by Gibbs [11] on the basis of analytical chemistry data, which represent the three major natural mechanisms controlling surface water chemistry as indicated in Figs. 5, 6, 7. In order to make these domains clear, Kumar [16] delineated the boundaries of the rock-water interaction dominance field, which were also adopted by other researchers [12]. For clarity in this study, these boundaries are presented by the boundaries  $K^+$  on the Gibbs cation diagram (Figs. 5a, 6a, 7a) and  $K^-$  on the Gibbs anion diagram (Figs. 5b, 6b, 7b). As in the Piper diagram, the number symbols in the figures correspond to the locations of the observation wells in Fig. 1. The circles and the non-circular symbols indicate dry and rainy season data, respectively. From these figures, almost all of samples in both seasons of three years fall in the boundaries  $K^+$  and  $K^-$ , which suggests that rock-water interaction is the major source for dissolved ions in PCA. Interestingly, samples from well No 7 in these years and well No 61 in the rainy season of 1993 show the highest TDS but very low weight ratios  $Cl/(Cl+HCO_3)$ , and thus fall outside  $G^+$ ,  $G^-$ , and  $K^+$ ,  $K^-$  boundaries. The anthropogenic activities such as irrigation, industrialization and urbanization may be the reason for very high TDS of these samples. In general, there are no significant changes in the weight ratios  $Na/(Na+Ca)$ ,  $Cl/(Cl+HCO_3)$  and TDS between the dry and rainy seasons as well between the two periods (from 1993 to 2003 and from 2003 to 2011).



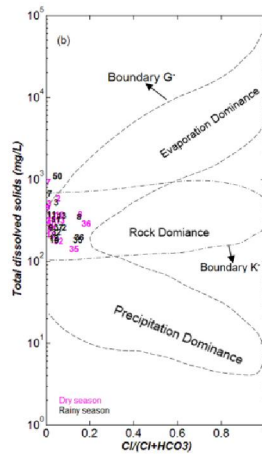
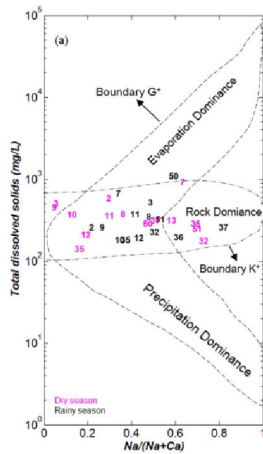


Figure 5. Gibbs diagrams for groundwater in 1993

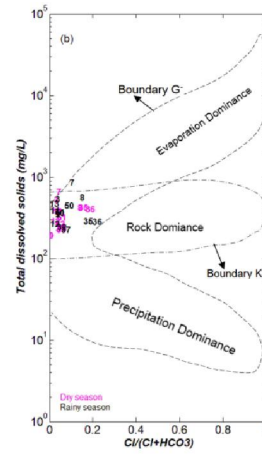
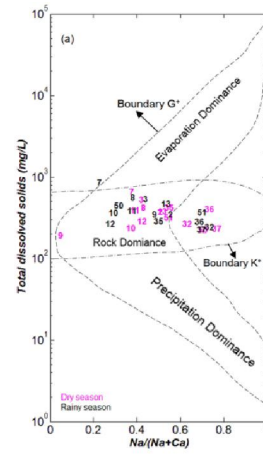


Figure 6. Gibbs diagrams for groundwater in 2003

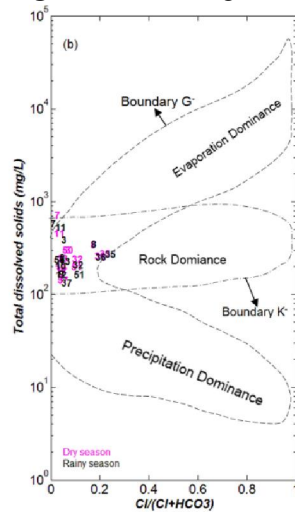
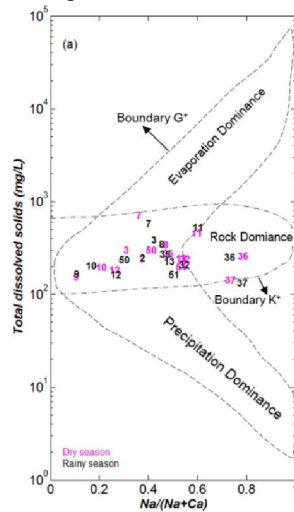


Figure 7. Gibbs diagrams for groundwater in 2011

## 5. Conclusions

The main objectives of this study are to investigate the decadal change in hydrogeochemical facies and to determine factors governing water chemistry of groundwater in PCA. In this paper, taking advantage of the unique database, hydrochemical parameters from 15 sampling PCA wells in Hanoi acquired during dry and rainy season in 1993, 2003 and 2011 were comprehensively analyzed. From analysis of the Piper diagrams for 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 15 PCA observation wells is of the  $[HCO_3^-]$  type during the dry and rainy seasons. Results from the Piper diagram indicated the decadal changes in the hydrogeochemical facies of at least 30% the sampling wells for dry and rainy seasons. The changes were particularly pronounced in the cation-type facies, while the anion-type facies remained almost unchanged. Moreover, the results also show that there are more

groundwater samples showing the changes in the hydrogeochemical facies during the period of 2003 – 2011 than during the period of 1993-2003. Although the Gibbs diagrams suggested that rock weathering is the main processes in the evolution of chemical composition of groundwater in the study area, contemporary anthropogenic activities, such as irrigation, industrialization and urbanization perhaps affect groundwater chemistry in the study area, leading to the decadal changes of hydrogeochemical facies. The findings of this study provide valuable information regarding the groundwater hydrogeochemical properties and hydrodynamics in Hanoi, Vietnam.

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