Analysis of the hydro-chemical characteristics and origin of the karst groundwater, East Jinan city

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Abstract. Understanding of the hydrochemical characteristics of the groundwater provides insight into the interaction of water with the environment. In this study, twenty-four groundwater samples were collected from study area analysed for various chemical parameters such as pH, K\textsuperscript{+}, Na\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, SO\textsubscript{4}\textsuperscript{2-}, HCO\textsubscript{3}-, Cl\textsuperscript{-}, TDS, TH. The objective of the study was to determine the groundwater hydrochemical facies and the main hydrochemical processes of governing the groundwater chemistry. The groundwater samples fall within the Ca-Mg-HCO\textsubscript{3} and Ca-Mg-Cl type in Piper trilinear diagram. Water-rock interaction and anthropogenic activities appear to be the major processes controlling the groundwater chemistry.

1. Introduction
Karst groundwater plays an important role in industrial and agricultural production and social development in Jinan, with the advantage of the abundant water quantity. Unfortunately, overexploitation of karst groundwater and participation of anthropogenic activities have resulted in the decline of karst water quality. The study of groundwater chemical characteristics will contribute to the groundwater quality evaluation \cite{1}, and it is also significant for the management of regional groundwater resources. The formation of karst groundwater chemistry depends on precipitation, general geology, weathering degree of different rock types, quality of recharge water and inputs from sources other than water-rock interaction \cite{2}. Through the study of the hydrochemical characteristics and causes of the regional groundwater, the interaction mechanism of the groundwater and the environment can be better revealed, and the scientific basis for the management of groundwater resources can be provided \cite{3}. Analyzing the hydrochemical evolution in aquifers will conduces to understand the nature of rock aquifers, geochemical processes governing water-rock interactions, as well as information of groundwater flow properties, such as residence time and hydraulic conductivity \cite{4, 5}. It has been proved that the study on groundwater hydrochemical characteristics is a powerful tool to understand the hydrochemical processes of carbonate aquifers \cite{6}.

2. Overview of the study area
Geographically, the study area is located in the eastern of Jinan, with the north boundary of Xiaoqing river. The study area belongs to the temperate continental climate, with the annual temperature of 14.3°C, and with the average annual rainfall of 670mm. Jinan is a monoclinic structure based on Paleozoic metamorphic rocks and develops a series of fault structures. Taking into account the special
structure, the Jinan’s karst groundwater system was divided into five subsystems. The study area is across the Jinan spring area and the white spring field, with a large scale NNW strike in the Dongwu fault, which is the division between Jinan spring area and white spring area. On the whole, dongwu fault is a water blocking fracture, only partially weakly permeable in the north, and it is the western boundary of the white spring catchment and the east boundary of Jinan spring catchment. There are also smaller scale F1 fracture and F2 fracture.

Most of the study area is covered by Quaternary strata, and Ordovician limestone is buried under the Quaternary sediment, with the sporadic distribution of limestone exposed in the south, while the magmatic rocks (diorite and gabbro) formed in the Mesozoic Yanshan Orogeny are distributed in the north, and most of them are covered by Quaternary sediment. There are the loose rocks group of porewater and carbonate rocks group of fracture karst water in the study area. The main types of groundwater are the Quaternary loose porewater and the carbonate fracture - karst water. This paper will mainly focus on the karst groundwater. The lithology of the carbonate aquifer is medium and thick leopard porphyry limestone, muddy limestone and dolomitic limestone, which was hidden in the quaternary, and was located in the drainage area of groundwater runoff. In the area where karst fractures develop, it has a large water inflow, which can reach more than 5000m$^3$/d. According to the collected field experiment results and the dynamic monitoring data of the groundwater level, there was no water-repellent layer between the karst aquifer and the pore water aquifer, which has close hydraulic connection. The cause of white spring is that the underlying karst water replenishes the quaternary pore water under the head pressure. Since the weaker permeable water of the quaternary pore water comparing with the karst aquifer, there was no phenomenon of spring water spewing, but showing a surface seepage.

Figure 1. Hydrogeological condition and location of sampling wells in study area

3. Sampling and analysis
There are 24 sampling wells in the study area, as shown in Fig. 1, of which W09 is an artesian well and the rest are closed production wells, which are karst water coming from the Ordovician limestone aquifer. Sampling directly from the outlet of the artesian well. However, for closed production wells, water samples are taken from the water outlet valve of the pump room. Pumping for a period of time
to remove residual water from the pipe before sampling, until the fresh water appears. Sampling containers were 2L PVC bottles, which were washed with groundwater for 2~3 times before sampling. The conventional ionic components of groundwater samples collected from study area were analyzed and tested, which including Sodium (Na\(^+\)), Potassium (K\(^+\)), Calcium (Ca\(^{2+}\)), Magnesium (Mg\(^{2+}\)), Bicarbonate (HCO\(_3^-\)), Carbonate (CO\(_3^{2-}\)), Sulphate (SO\(_4^{2-}\)), Chloride (Cl\(^-\)), Total dissolved solids (TDS) and Total Hardness (TH). PH value was measured using the pH meter (CT-6023) in the field and Na\(^+\), K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) were tested in laboratory using the flame atomic absorption spectrometry by Atomic absorption spectrophotometer (YQ003), and HCO\(_3^-\), CO\(_3^{2-}\), SO\(_4^{2-}\), Cl\(^-\) were tested using spectrum analysis method by UV Spectrophotometer (YQ059). The hydrogeochemical data obtained from the test were processed, the piper diagram was drawn by AqQA, and Gibbs diagram was plotted using the Origin software. Statistical analysis (Table 1) were conducted by Spass software.

4. Results and discussion

4.1. General groundwater chemistry

The cations in the chemical components of karst water are mainly calcium ions, of which half of the samples were calcium water type and remaining 33.3% of samples located at the center of the ternary plot, which were regarded as no dominant type, while the another remaining 16.7% of them were sodium and potassium water type. Among all the samples, 83.3% of them plotted on the zone, representing the alkaline earths exceed alkalies. The concentration of alkaline earth metal Ca and Mg range from 11.90 to 231.61mg/l and 17.50 to 51.56mg/l, with a mean of 92.19mg/l and 27.80mg/l, respectively. The concentration of alkaline metals Na and K are 17.42~92.00mg/l and 0.49~5.26mg/l, as well as a mean of 52.92mg/l and 1.71mg/l, respectively.

For the anions, HCO\(_3^-\) accounts for the majority, and the concentration of anions decreased in sequence was HCO\(_3^-\) > SO\(_4^{2-}\) > Cl\(^-\). The concentration range of three anions were 214~500.12mg/l, 40.43~233.00mg/l and 37.60~220.01mg/l, with the mean of 299.28, 115.59, 97.79mg/l, respectively. Nearly half of the samples (45.8%) belong to the bicarbonate type, while the remaining were plotted on the no dominant anion zone. Almost the same proportion of samples fall down the weak acids exceed strong acids zone and strong acids exceed weak acids zone.

| Parameters     | Range   | Median | Mean  | SD    | Kurtosis | Skewness | Coefficient of Variation |
|----------------|---------|--------|-------|-------|----------|----------|-------------------------|
| Sodium         | 17.42-92.00 | 54.00 | 52.92 | 23.84 | -1.25    | 0.04     | 0.45                    |
| Potassium      | 0.49-5.26 | 1.25  | 1.71  | 1.22  | 1.24     | 1.30     | 0.71                    |
| Calcium        | 11.90-231.61 | 81.46 | 92.19 | 68.58 | -1.27    | 0.48     | 0.74                    |
| Magnesium      | 17.50-51.56 | 24.60 | 27.80 | 8.63  | 1.31     | 1.37     | 0.31                    |
| Bicarbonate    | 214-500.12 | 288.50 | 299.28 | 72.32 | 0.73     | 0.97     | 0.24                    |
| Sulphate       | 40.43-233.00 | 103.48 | 115.59 | 49.12 | 0.16     | 0.69     | 0.42                    |
| Chloride       | 37.60-220.01 | 81.85 | 97.79 | 50.48 | 0.40     | 1.14     | 0.52                    |
| pH             | 7.16-7.72 | 7.49  | 7.45  | 0.16  | -0.10    | -0.29    | 0.02                    |
| TH             | 340-741.13 | 448.64 | 493.71 | 125.55 | -1.30    | 0.49     | 0.25                    |
| TDS            | 428-1082  | 681   | 704.13 | 216.40 | -1.31    | 0.37     | 0.31                    |
4.2. Hydrochemical facies
Graphical representations of the concentration of the main dissolved components (mainly anions and cations) in groundwater will contribute to understand the evolution, grouping and distribution of groundwater chemical components.

![Box-whisker Plot of the chemical parameters](image1)

Figure 2. Box-whisker Plot of the chemical parameters
Piper trilinear diagram [7] consists of two triangles and one diamond. Three sides of the lower left triangle represent the milliequivalent percentages of Na+K, Ca and Mg in the cation, respectively. The three sides of the lower right triangle represent the milliequivalent percentage of HCO₃, Cl, and SO₄. The anions and cations are shown by separate ternary plots, which were projected onto a diamond. Water samples shown on the Piper diagram can be grouped in hydrochemical facies. The Gibbs Diagram [8] was widely used to reveal the relationship between groundwater components and aquifer lithology. In Gibbs diagram, scatter plots were plotted with Cl/(Cl+HCO₃) and (Na+K)/(Na+K+Ca) as the abscissa and Total Dissolved Solids as the ordinate. In the figure, it was divided into three different regions, which are the precipitation dominant region, the evaporation dominant region and the water-rock interaction dominant region. As shown in Gibbs diagram, most of the water samples in this paper fell in the Gibbs diagram. The regional and evaporative dominant regions, where the water-rock interaction dominates, indicate that there is a significant interaction between the petrochemical properties of the groundwater system and groundwater chemistry.

![Piper trilinear diagram of the groundwater chemistry](image2)

Figure 3. Piper trilinear diagram of the groundwater chemistry
From the Piper trilinear diagram and the Gibbs diagram, we can conclude that the karst water in the study area accounts for 37.5% (9 of all samples) and Ca-Mg-Cl accounted for 45.9% (11 of all samples) for Ca-Mg-HCO$_3$. Silicate weathering and water-rock interaction are important factors in increasing the concentration of major ions in groundwater. The chemical composition in groundwater is the product of long-term interaction between groundwater and the environment and human activities. The changes in groundwater composition reacted with the surrounding rocks, and the chemical compositions were exchanged when the atmosphere, the hydrosphere, and the biosphere took place the water exchange. A large number of unreasonable human activities also affected the chemical compositions of groundwater [3]. The groundwater in study area is dominated by Ca-Mg-HCO$_3$ and Ca-Mg-Cl, which indicate that the major hydrochemical process is weathering-solubilization. The formation of groundwater type is mainly the dissolution of aluminosilicate, carbonate and evaporating salt rock.

Figure 4. Gibbs diagram of the groundwater samples

Groundwater chemical components are characterized by water-rock interactions and chemical processes. Therefore, groundwater chemistry can be used to identify water-rock or water chemical processes. In general, water-rock interactions can be characterized by plotting TDS vs. Na/(Na+Ca) and TDS vs. Cl/(Cl+HCO$_3$), which was named as Gibbs diagrams (Gibbs, 1970). In Gibbs diagrams, the area where the samples fall into is divided into three parts, which are Evaporation dominant zone, Rock dominant zone, Precipitation dominant zone, respectively. In the evaporation dominance, the samples fall into the upper right corner of the Gibbs diagram. The TDS values are higher, as well as the Na/(Na+Ca) and Cl/(Cl+HCO$_3$). It indicates that the evaporation-sedimentation is the main factor of the chemical composition of groundwater. In the rock dominance, the samples fall to the left of the Gibbs diagram, with the moderate value of the TDS, while it has the smaller value of the Na/(Na+Ca) and Cl/(Cl+HCO$_3$). It shows that water-rock interaction is the main factor controlling the chemical composition of groundwater. In the precipitation dominance, the samples fall into the lower right side of the Gibbs diagram, the TDS value is lower, and the values of while Na/(Na+Ca) and Cl/(Cl+HCO$_3$) are higher. It indicates that atmospheric precipitation is the main factor controlling the composition of groundwater chemical components. There are the distribution characteristics of karst water on the Gibbs diagram in study area, as shown in Figure 4.a, Figure 4.b. It can be seen that the chemical compositions of groundwater in study area was mainly affected by water-rock action and evaporation-sedimentation.

5. Conclusions

Samples collected from the study area are characterized by high concentration of Ca$^{2+}$, HCO$_3^-$ and SO$_4^{2-}$. Groundwater has been classified as Ca-Mg-HCO$_3$, Ca-Mg-Cl, Na-Cl, Na-HCO$_3$-Cl type, which
is dominated by Ca-Mg-HCO₃ and Ca-Mg-Cl type. It indicates that the major hydrochemical process is weathering-solubilization and water-rock interaction.

The factors affecting the types of karst water are: (1) the influence of topography and landform, the terrain in the southern mountainous area is relatively high, the karst water directly receives the atmospheric precipitation recharge, the hydraulic gradient is large, the water alternates strongly, and the mineral group in the aquifer is easy. The karst water in the southern mountainous area is dominated by HCO₃-Ca type, while the low-lying river valley and the northern pressure-bearing area are mostly HCO₃-Ca·Mg type water. (2) Influence of stratum lithology, the mineral components of regional karst water system limestone are mostly calcite, dolomite, gypsum, etc., and exposed in the southern mountainous area, and affected by topography and landform, due to atmospheric precipitation, CO₂ and the result of the interaction and migration of karst water with the mineral components of the aquifer, so that the karst water has a specific type of water chemistry. (3) The chemical composition and content of karst water are closely related to geological environment and dissolution. The dissolution is related to the mineral composition, topography, landform and hydrodynamic conditions of the aquifer. As the migration distance and burial depth increase, the dissolved ion content in the water increases, the mineralization degree increases, and Ca²⁺ gradually reaches saturation and precipitates, so the content of Mg²⁺ is relatively increased, so the karst water type in the pressure-bearing area is HCO₃-Ca·Mg type.

Acknowledgments
This work was financially supported by the Shandong Provincial Natural Science Foundation, China (ZR2014DM011), Shandong provincial key research project, China (2015GSF117025) and Migration and transformation model of groundwater chlorinated hydrocarbons in the eastern urban area of the sponge city water system in Jinan city research project (2016JSFW02Z0307).

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