Hydrochemical Types of Karst Groundwater in Tailai Basin

Jianguo Feng, Deshuai Ji, Zongjun Gao, Tongmin Lu and Minghao He

College of Earth Science and Engineering, Shandong University of Science and Technology, Qingdao, China.
*Email: fengjianguo20316@sohu.com

Abstract. Karst water resources is about 24% of the total amount of groundwater resources that can be exploited in China. Among the 15 groundwater sources in Tailai Basin, there are 12 karst water sources, accounting for 80%. With the survey and evaluation data of groundwater sources in Shandong Province, hydrochemical types analysis of karst water is carried out by Schukalev classification and The trilinear chart by Piper, and it is of great significance to development and utilization of karst water. The hydrochemical types of karst water is dominated by HCO$_3$$\cdot$SO$_4$-Ca water. However, if the naming of hydrochemical types involve nitrate, excess 39% of the karst water hydrochemical types changes. In addition, historical data shows that the concentration of nitrate in karst water has gradually increased, so it is recommended to increase nitrate indicators in the classification of hydrochemical types.

The type of groundwater hydrochemical is the concentrated reflection of groundwater chemical composition and one of the important contents of the study of groundwater hydrogeochemical characteristics. In China, the distribution of karst water is extensive, which plays an important role in solving some urban, industrial and agricultural water problems. The chemical characteristics of karst water are mainly affected by aquifer lithology, groundwater burial conditions, human activities, etc. Many experts and scholars at home and abroad have carried out special research in related fields.

In the Tailai Basin described in this paper is bounded by the Taishan Mountains in the north, the Mengshan Mountain and the remaining veins in the south, the Lushan Mountain in the east, and the east bank of the Dongping Lake in the west. Its extreme geographical coordinates are: east longitude 116°20′52″—117°58′57″, north latitude 35°43′05″—36°34′15″, area 8173 km$^2$, administrative divisions belong to Tai'an City and Jinan City.

1. Hydrogeological Conditions of Karst Water

1.1. Carbonate Fractured Karst Water

The aquifer group consists of the Middle Ordovician and the Upper Cambrian Fengshan Formation limestone, dolomitic limestone and argillaceous limestone developed in the fractured karst, mostly distributed in the north of each fault block, and the exposed area Most of them are low hills. Until the mountain slope is buried or concealed under the Carboniferous, Permian and Mesozoic and Cenozoic, the limestone is thick and widely distributed, its fractured karst develops, connectivity is strong, groundwater hydraulics Close contact. However, due to the influence of structure, geomorphology and lithology conditions, the occurrence and water-richness of groundwater are very different. Generally, the water yield property in the bare area is poor, and the water yield of a single well is less than 500 m$^3$/d; the water yield property in the buried area is good, the water yield of a single well is 500-2000 m$^3$/d, the karst development is weakened with the increase of the burial depth, and the water yield property is relatively poor; in the Quaternary concealed area, the water yield property is strong, and
the water yield of a single well is generally 1000-5000 m$^3$/d, which can often form a water-rich section or a strong water-rich zone with water supply significance. Under the mining conditions, the hydraulic connection between the fractured karst water in these areas and the Quaternary pore water in the upper part is very close, and the Quaternary pore water often becomes the main source of supply for the fractured karst water. The Quaternary sand gravel layer in the water source areas of Tai’an City, Jixian Township, Niuquan town, Fangxia town and other water sources directly contact with limestone to form a “skylight”.

1.2. Carbonate Rock Clastic Rock Karst Fissure Water
The aquifer is composed of the limestone shale from the Lower Cambrian Shantou Formation to the Upper Cambrian Changqing Formation, and is mostly distributed in the north of the fault block and the northern edge of the basin. Due to the limestone and shale interbedded thin layer of limestone interbed, the groundwater recharge conditions are poor, the fractured karst is not developed, the water yield property is weak, and the water yield of a single well is generally less than 500 m$^3$/d. In the thick limestone distribution area of Shantou Formation and Zhangxian Formation, the fracture karst is relatively developed, and the water-rich water is relatively strong. The water yield of a single well is more than 1000 m$^3$/d.

2. Characteristics of Hydrochemical Types of Karst Water

2.1. Statistics of Water Quality Test Results
In September 2017, 90 samples of karst water were taken. The statistics of 10 indicators including pH, K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$, SO$_4^{2-}$, HCO$_3^-$, NO$_3^-$, and total dissolved solids are shown in Table 1.

| Number | Detection index | Min  | Max  | Mean  | Std  |
|--------|-----------------|------|------|-------|------|
| 1      | pH              | 6.90 | 8.10 | 7.49  | 0.20 |
| 2      | K$^+$           | 0.20 | 8.33 | 1.41  | 1.44 |
| 3      | Na$^+$          | 3.67 | 253.85 | 27.59 | 31.61 |
| 4      | Ca$^{2+}$       | 33.87 | 529.26 | 150.30 | 66.59 |
| 5      | Mg$^{2+}$       | 1.46 | 78.99 | 25.44 | 11.18 |
| 6      | Cl$^-$          | 8.51 | 274.76 | 63.96 | 49.06 |
| 7      | SO$_4^{2-}$     | 18.25 | 1025.44 | 151.43 | 137.82 |
| 8      | HCO$_3^-$       | 55.20 | 484.56 | 276.28 | 88.91 |
| 9      | NO$_3^-$        | <0.01 | 443.90 | 83.99 | 64.95 |
| 10     | STD             | 185.00 | 2785.00 | 657.59 | 329.57 |

2.2. Hydrochemical Types
Groundwater has different classification methods according to its chemical composition, most of which are divided by the relative content and relationship between anions and cations, such as Shukalev classification and The trilinear chart by Piper, etc. The hydrochemical type of each karst water sample was calculated by programming, and the statistics were shown in Figure 1.
In the 90 water samples of karst waters, there are 11 types of groundwater hydrochemical, including 33 HCO$_3$•SO$_4$•Ca waters, accounting for 36.67% of the karst water samples. And there are 20 HCO$_3$•Ca water, accounting for 22.22% of the quantity of karst water samples. In terms of anions, there are 86 water samples with milligram equivalent percentage of bicarbonate over 25%, accounting for 95.56% of the total karst water samples. There are 62 water samples whose milligram equivalent percentage of sulfate is more than 25%, accounting for 68.89% of the total karst water samples. And there are 23 water samples with the milligram equivalent percentage of chloride over 25%, accounting for 25.56% of the total karst water samples. In terms of cations, there were 90 water samples with the milligram equivalent percentage of calcium over 25%, accounting for 100.00% of the total number of karst water samples. There are 14 water samples whose milligram equivalent percentage of magnesium is more than 25%, accounting for 15.56% of the total karst water samples. And there are 2 water samples whose sodium milligram equivalent percentage is more than 25%, accounting for 2.23% of the total karst water samples.

According to the statistical table of hydrochemical types of karst water, the proportion of the top three hydrochemical types of karst water in the Tailai Basin is more than 70%, and the proportion of HCO$_3$•SO$_4$•Ca water is the largest. Secondly, the percentage of HCO$_3$•Ca water in the quantity of karst water types is the second. The percentage of HCO$_3$•SO$_4$•Cl-Ca water in the quantity of karst water types ranks the third (Table 2).

According to the statistical analysis of the proportion of the hydrochemical types of different ions in karst water, bicarbonate and sulfate are the main anions, and the proportion of the two is relatively close; in terms of cations, calcium dominates.

**Table 2. Statistics of Karst Groundwater Hydrochemical Types for different ions**

| Item     | HCO$_3$ | SO$_4^{2-}$ | Cl$^-$ | Ca$^{2+}$ | Mg$^{2+}$ | Na$^+$ |
|----------|---------|-------------|--------|-----------|-----------|--------|
| Quantity | 86      | 62          | 23     | 90        | 14        | 2      |
| Percentage | 95.56  | 68.89       | 25.56  | 100       | 15.56     | 2.23   |

The trilinear chart by Piper visually shows the hydrochemical characteristics of karst water in the Tailai Basin (Figure 2). If the water sample point falls in the diamond zone 1, the content of alkaline earth metal ions Ca$^{2+}$ and Mg$^{2+}$ exceeds the alkali metal ion K$^+$ and Na$^+$ content. Water sample points appeared in both the zone 3 and the zone 4, and most of them were in the zone 3, indicating that most of the water samples had weak acid roots HCO$_3$ exceeding the strong acid roots SO$_4^{2-}$ and Cl$^-$. 
3. **Analysis of Hydrochemical Types of Karst Water**

During data analysis, it was noted that the NO$_3^-$ concentration of water sample no. J026 was 443.90 mg/L, and the average value of NO$_3^-$ concentration of all karst water samples was 83.99 mg/L, and the high concentration of NO$_3^-$ concentration may be related to the transitional application of nitrogen fertilizer. Therefore, NO$_3^-$ is considered to be introduced into the hydrochemical type of karst water.

After adding NO$_3^-$ in the anion to participate in the naming of hydrochemical types, the milligram equivalent percentage of bicarbonate, sulfate and chloride all decreased to varying degrees, and the naming of a total of 28 water samples changed, covering 31.1% of the total water samples.

As a result of the participation of NO$_3^-$ in naming, groundwater hydrochemical types change as follows:

1. Some of the anions participating in the naming cannot participate in the naming because the milligram equivalent percentage is less than 25%. For example, in B10 water sample, the milligram equivalent percentage of bicarbonate was changed from 43.96% to 33.22%; the milligram equivalent percentage of sulfate was changed from 29.50% to 22.28%; the milligram equivalent percentage of chloride was changed from 26.53% to 20.08%; and the milligram equivalent percentage of nitrate was 24.42%. The hydrochemical type is changed from HCO$_3^-$•SO$_4^-$•Ca water to HCO$_3^-$•SO$_4^-$•Ca water. The B24 water sample was changed from HCO$_3^-$•SO$_4^-$•Cl•Ca water to HCO$_3^-$•SO$_4^-$•Ca water.

2. Some of the anions participating in the naming are replaced by NO$_3^-$. For example, in the case of B9 water sample, the hydrochemical type without considering NO$_3^-$ is HCO$_3^-$•SO$_4^-$•Ca•Mg water, the milligram equivalent percentage of bicarbonate is 44.83%, the milligram equivalent percentage of sulfate is 31.97%; After adding NO$_3^-$, the milligram equivalent percentage of bicarbonate is 25.45%, the milligram equivalent percentage of sulfate is 18.14%, the milligram equivalent percentage of nitrate is 43.23%, and the water chemical type is changed to HCO$_3^-$•NO$_3^-$•Ca•Mg water. The B42 water sample was changed from HCO$_3^-$•SO$_4^-$•Ca water to HCO$_3^-$•SO$_4^-$•NO$_3^-$•Ca water.

4. **Conclusion**

(1) The hydrochemical type of karst groundwater in Tailai basin is mainly HCO$_3^-$•SO$_4^-$•Ca water. The sum of HCO$_3$•SO$_4$•Ca water, HCO$_3$•Ca water and HCO$_3$•SO$_4$•Cl•Ca water accounts for 71.11% of the total karst water, indicating that the water-bearing system of karst water determines the hydrochemical characteristics of karst water to some extent.

(2) In karst water of Tailai basin, the anions are mainly bicarbonate and sulfate, and the proportions...
of the two are relatively close; Cations are calcium dominated absolutely.

(3) After 2000, the concentration of anion components in karst water, such as bicarbonate, sulfate, chloride and nitrate, increased significantly. The proportion of nitrate in anion in karst water cannot be ignored, which has an important influence on the type of hydrochemical, and it is suggested that nitrate index should be added into the classification of hydrochemical in the future.

(4) If nitrate is used as the classification index of hydrochemical types, how to express hydrochemical types in the form of symbols and graphs and theoretically reflect the different characteristics of different types still needs further work.

5. Acknowledgement

Groundwater source survey and evaluation of Shandong Province (SDZS-2016-GTT02).

6. References

[1] Dong W H, Su X S, Hou G C, Lin X Y and Liu F T 2007 Distribution Law of Groundwater Hydrochemical Type in the Ords Cretaceous Artesian Basin Journal of Jilin University(Earth Science Edition) 37 288-292.

[2] Feng J G 2003 Hydrochemical Type Classification-A Case Study of Cretaceous Huanhe Group Groundwater of Ords Basin Chang'an University.

[3] Zhou X and Ye Y H 2014 Improvement and Application of Schukalev Groundwater Hydrochemical Classification Method: taking Groundwater in Jinjiang City, Fujian Province as an Example Resources Survey and Environment 35 299-304.

[4] Liang Y P and Wang W T 2010 The Division and Characteristics of Karst Water Systems in Northern China Acta Geoscientica Sinica 31 860-868.

[5] Liang X, Zhang R Q, Niu H, Jin M G and Sun R L 2012 Development of the Theory and Research Method of Groundwater Flow System Geological Science and Technology Information 31 143-151.

[6] Zhang Y, Dong W H, Li M Z, Zheng Z X, Shi X F and Guo Z X 2011 Study on Distribution Characteristics of TDS and Hydrochemical Type of Shallow Groundwater in Henan Plain JOURNAL OF CHINA HYDROLOGY 31 79-83.68.

[7] Ye Y H, Zhou X and Liu L 2015 Evolution and genesis of groundwater hydrochemical types in Yingtian of Jiangxi Journal of Guilin University of Technology 35 269-273.

[8] Claudio E M, Matthias R, Mauricio T and Malcolm E C 2015 Hydrochemical evolution and groundwater flow processes in the Galilee and Eromanga basins, Great Artesian Basin, Australia: A multivariate statistical approach Science of The Total Environment 508 411-426.

[9] Yue D D and Su X S 2016 Distribution Law of TDS and Groundwater Hydrochemical Type in the Downstream Plain of Yishu River water saving irrigation 41 77-80.

[10] Yang Q C, Wang L C, Ma H Y, Yu K and Martin J D 2016 Hydrochemical characterization and pollution sources identification of groundwater in Salawusu aquifer system of Ords Basin, China Environmental Pollution 216 340-349.

[11] Song C, Wang P, Han G L and Shi Y C 2017 The hydro-chemical characteristics of shallow groundwater in loess tableland and its implication to carbon cycle South-to North Water Transfers and Water Science & Technology 15 121-126

[12] Wang H F, Wang H Y, Li C Y and Mu Z 2017 Distribution of hydrochemical type and genesis of pollutant of groundwater in Handan city Journal of Hebei University of Engineering (Natural Science Edition) 34 53-56,65.

[13] Cansu Y and Sakir S 2017 Hydrogeological and hydrochemical studies of the Kaman-Savcili-Büyükoba (Kirsehir) geothermal area, Turkey Geothermics 65 99-112.

[14] Chafouq D, Maudour A E, Elgettafi M, Himi M, Chouikri I and Casas A 2018 Hydrochemical and isotopic characterization of groundwater in the Ghis-Nekor plain (northern Morocco) Journal of African Earth Sciences 139 1-13.

[15] Liu R F 2006 The Feature of Water Environment Evolvement of the Dawen River Basin and the Appraiseement of Its Influence to the East Route of the South to North Water Transfer Project Qingdao: Shandong University of Science and Technology,2006.
[16] Li B 2007 Study on the Groundwater Environment Simulation of City’s Wellfield and the Countermeasure of Feeding Water Supplement Tai’an: Shandong Agricultural University.

[17] Zhang Z X, Zhu Z H, Liu C E and Luo F 2014 Predication on Water Quality Evolution of Typical Karst Groundwater Source Area in Shandong Province Land and Resources in Shandong Province 30 29-33,38.

[18] Wei X Y, Zhang B X, Li W L, Liu D M and Zhang J S 2015 Research on the Numerical Simulation of Karst Groundwater in Feicheng Basin China Rural Water and Hydropower 59-64.

[19] Zhang R Q, Liang X, Jin M G, Wan L and Yu Q C 2011 Foundation of Hydrogeology Beijing: Geological Publishing House 66-69.

[20] Gao Z J, Zhang H Y, Sun M X, Xu H B and Yao D X 2017 The chemical characteristics and causes of shallow groundwater in the Rizhao coastal area of Shandong province are discussed Ground water 39 1-4.

[21] Wang Z L, Gao Z J, Xu Y and Li L 2013 Hydrochemical Characteristics of Karst Water in Jinan Spring Region Land and Resources in Shandong Province 29 27-29.

[22] Gao Z J, Sun W G Tang M S, Wu X L, Liu M, Han Y L and Cheng C L 2001 Relation between Karstic Water Exploitation and Geological Environment in Tai’an -Jixian Water Source Area Geology of Shandong 17 86-91.

[23] Liu L C, Chen H H, Ma Z M and Gao Z J 2003 Simulation and analysis of karst water environmental system in Taian city Journal of Hydraulic Engineering 107-111,116.

[24] Wang M and Gao Z J 2009 Study on Groundwater Environment in Dongwu Water Sources Area, Taian City Based on GMS Journal of Shandong University of Science and Technology (Natural Science Edition) 28 20-24.