PAPER • OPEN ACCESS

Study on Hydrochemical Characteristics in Jinan Spring Catchment

View the article online for updates and enhancements.

Study on Hydrochemical Characteristics in Jinan Spring Catchment

Xinhui Zhang, Liting Xing [*], Yanan Dong, Xiaoxun Lan, and Qianqian Cao

School of Water Conservancy and Environment, University of Jinan, Jinan, China

*Corresponding author e-mail: 1396796523@qq.com

Abstract. In this paper, 50 sets of groundwater samples were collected in Jinan spring catchment, and SPSS was used for factor analysis, as well as piper diagram and ion ratio method for comprehensive analysis. The hydrochemical characteristics and influencing factors of spring water in Jinan spring catchment were studied. The analysis results show that the hydrochemistry type of the spring area is mainly HCO_3-Ca or $HCO_3 \cdot SO_4$-Ca and the groundwater in the spring area is mainly affected by the weathering of rock minerals such as carbonate rock, halite and sulphate rock, and the influence of human activities should not be ignored. It is of great significance to clarify the cause of hydrochemistry in Jinan spring and to protect the spring environment.

1. Introduction

As a typical karst spring in the north, Jinan Springs has been crowned in the world since ancient times, and its legendary style is different. However, in recent years, with the acceleration of urbanization and industrialization, under the influence of the expanding scope of human activities, indicators such as Cl^-, SO_4^{2-}, NO_3^-, salinity and total hardness have continued to rise.The karst groundwater is polluted to varying degrees in its direct recharge area, indirect recharge area and discharge area, and the quality of karst water in the spring area is deteriorating[1-5]. At present, many experts and scholars at home and abroad have studied the hydrodynamic field characteristics of Jinan spring catchment[6-9]. For the hydrochemical characteristics of spring groundwater in Jinan spring catchment and spring water sources, mathematical statistics, ion ratio and principal component analysis are generally used. Factor analysis, cluster analysis, correlation analysis, piper diagram method and isotope method were analyzed[10,11].

Based on 50 sets of groundwater samples collected in Jinan Spring, the SPSS analysis, Gibbers diagram and Piper three-line diagram method were used to study the hydrochemical types of karst groundwater in Jinan spring catchment, and the chemical origin of Jinan spring water was explained. Protection has a certain effect.

2. Study Area

The Jinan spring catchment is located in the central and western part of Shandong Province. The research area belongs to the warm temperate continental monsoon climate. The average annual temperature is 14.3°C, the average annual evaporation is 1500~1900mm, the average annual precipitation is 676.94mm (1956-2013), and the precipitation is unevenly distributed during the year. The wet season is from June to September, and the average precipitation is 476.24mm, accounting for 73% of the annual precipitation. Jinan City is located in the northern margin of mountainous area in central Shandong Province,the terrain

is high in the south and low in the north. The southern part is a crystalline basement composed of pre-Sinian gneiss,and the Cambrian-Ordovician strata are exposed from the old to the new to the north. The magmatic rock mass is distributed in the north. Under this particular topography and geological structure, the karst water is replenished with atmospheric precipitation in the southern mountainous area. The direction of motion is roughly the same as the terrain slope direction and the trend direction of the stratum, and it is transported from south to north. When the karst water moves to the north, it encounters the magmatic rock mass and is blocked. The groundwater is enriched, and the pressurized water is exposed in the form of spring in suitable topography and favorable structural parts.

3. Methodology

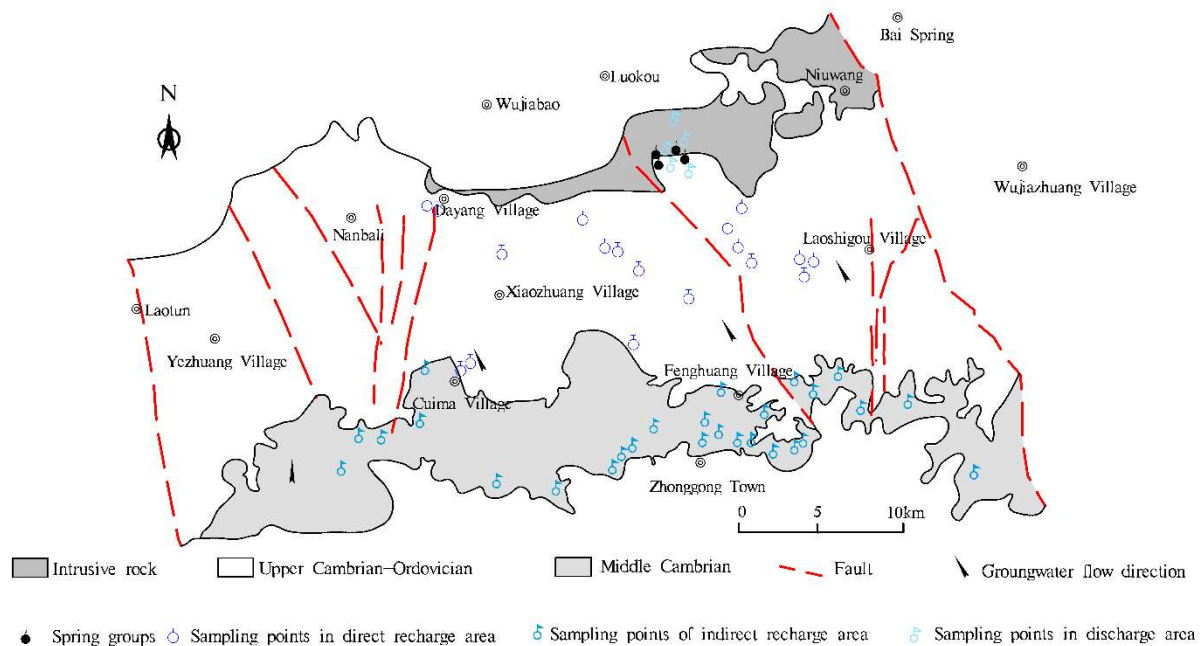### 3.1. Sampling and chemical analyisis

Figure 1. Distribution of Jinan spring catchment and groundwater sampling points

The sampling points are distributed in the Jinan spring catchment. The sampling time is May 2013. A total of 50 groundwater samples were collected (including:5groups in the discharge area, 18 in the direct recharge area, and 27 in the indirect recharge area). The sampling points are shown in Figure 1. The groundwater samples are collected, stored and sampled in strict accordance with the Technical Specifications for Groundwater Environmental Monitoring (HJ/T164-2004). The test method is shown in Table 1.

Table 1. Method for determination of various ion components in groundwater.

Test items	Determination method
K^+, Na^+, Ca^{2+}, Mg^{2+}	Flame atomic absorption spectrophotometry
Cl^-, HCO_3^-	Titration method
SO_4^{2-}, NO_3^-, F^-	Chromatography of ions
pH	Acidometer
COD	Potassium dichromate oxidation method
TDS, EC	Portable conductivity meter (field measurement)
TH	As $CaCO_3$

3.2. Data analysis

$$E = \frac{\sum N_c - \sum N_a}{\sum N_c + \sum N_a} \times 100\% \qquad (1)$$

Where E is the relative error; N_c, N_a represent the milliequivalent concentration (meq/L) of cation and anion, respectively.

The reliability test of the water sample data was carried out by using the anion-cation balance test method. The absolute value of the balance error E of the anion and cation was less than 5% as reliable data. All the data were verified as reliable data. In this study, the Piper diagram was used to analyze the hydrochemistry type and characteristics of groundwater samples. At the same time, factor analysis, Gibbs graphic method were used to analyze the cause of hydrochemistry.

4. Results and Discussion
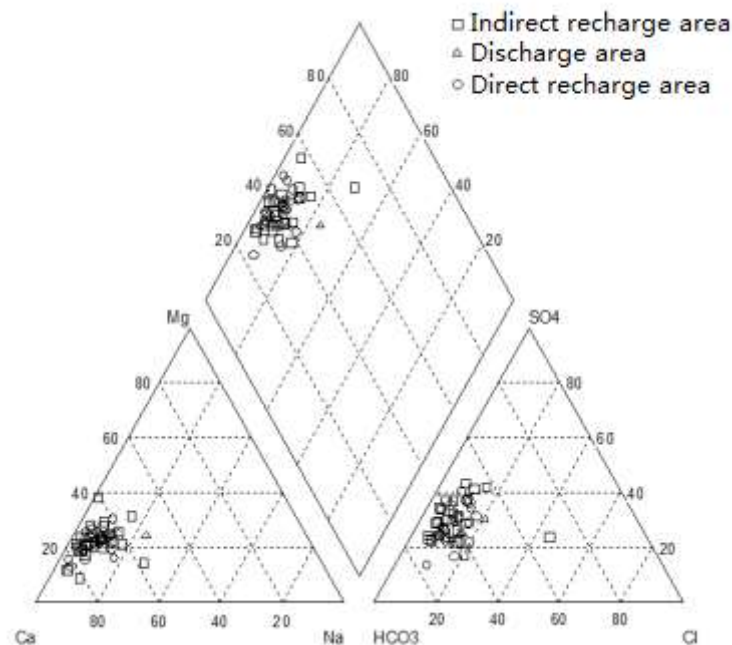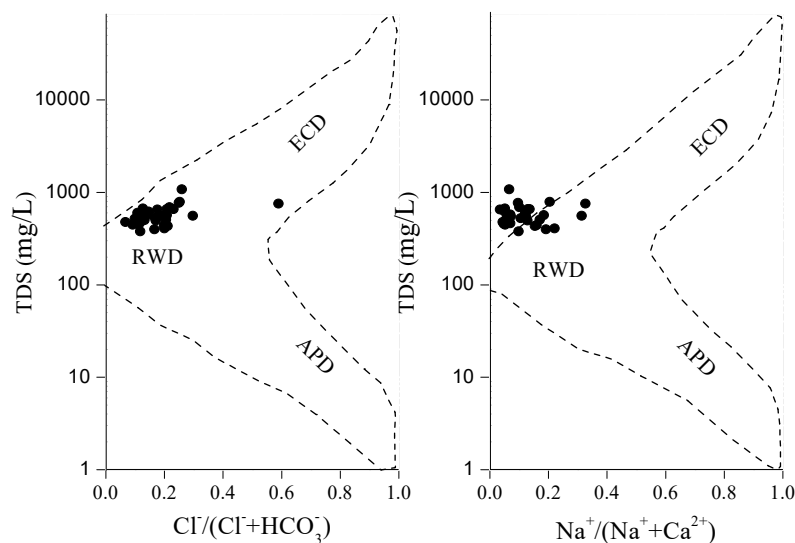
4.1. Hydrochemical type

Figure 2. Piper diagram of hydrochemical composition in the study area.

It can be seen from the Piper diagram that the groundwater hydrochemical characteristics of the study area are relatively stable and there is no obvious variation characteristics. In general, the types of hydrochemistry in the study area are mainly HCO_3-Ca and $HCO_3 \cdot SO_4$-Ca.

4.2. Genetic mechanism of hydrochemical components

4.2.1. Ion analysis based on Gibbs graph. The Gibbs diagram can visually see the formation of chemical components in surface water, and determine the main chemical components in the surface water of the region are affected by evaporation and concentration, rock and soil, and atmospheric precipitation [12-14]. The Gibbs diagram method can be used not only to analyze the ion origin of surface water, but also to analyze the ion origin of groundwater. The Gibbs plot is a plot of TDS as the Y-axis, $\gamma Na^+ / \gamma (Na^+ + Ca^{2+})$ and $\gamma Cl^- / \gamma (Cl^- + HCO_3^-)$ as the X-axis. In the Gibbs diagram, when the TDS value is low and the ratio of $\gamma Na^+ / \gamma (Na^+ + Ca^{2+})$ or $\gamma Cl^- / \gamma (Cl^- + HCO_3^-)$ is greater than 0.5, it indicates that the

hydrochemical composition of the region is mainly affected by atmospheric precipitation; TDS When the value is medium and the ratio of $\gamma Na^+ / \gamma$ ($Na^+ + Ca^{2+}$)or $\gamma Cl^- / \gamma$ ($Cl^- + HCO_3^-$) is less than 0.5, it indicates that the hydrochemical composition of the region is mainly affected by rock weathering; the TDS value is higher and When the ratio of $\gamma Na^+ / \gamma$ ($Na^+ + Ca^{2+}$)or $\gamma Cl^- / \gamma$ ($Cl^- + HCO_3^-$) is close to 1, it indicates that the hydrochemical component of the region is mainly affected by evaporation. It can be seen from the Gibbs distribution map of hydrochemistry in the study area (Fig.3) that atmospheric precipitation and evaporation concentration have little effect on the hydrochemical composition in the study area. The hydrochemical composition in Jinan spring catchment is mainly affected by rock weathering.

(Note: RWD indicates rock weathering; APD indicates atmospheric precipitation; ECD indicates evaporation and concentration)

Figure 3. Gibbs distribution map of groundwater hydrochemistry in the study area

4.2.2. Factor Analysis. According to the original data, the variance contribution rate, the cumulative variance contribution rate and the twiddle factor load matrix of the correlation coefficient matrix in Table 2. are calculated by SPSS software.

(1) The cumulative total variance contribution rate of the two principal components in the drainage area is 93.575%, including the information amount of 93.575% of the original chemical data (Table 2.). The variance contribution rate of the first principal component (PC1) is 57.05%, which is mainly related to K^+,Ca^{2+},HCO_3^-,NO_3^-, total hardness, COD, PH, and TDS. The ion scale coefficient results show that Cl^- and NO_3^- in karst water are mainly affected by human activities. The above ions have a high correlation with Ca^{2+}, and PC1 represents the influence of human activities on karst water.

The second principal component (PC2) is composed of K^+,Na^+,Mg^{2+},Cl^-,SO_4^{2-},F^-, COD, and PH, and the variance contribution rate is 36.525%. The contribution rate of Ca^{2+} to PC2 is second only to HCO_3^- and TDS. According to the ion proportional coefficient , Ca^{2+}, Mg^{2+} and HCO_3^- ions in karst water are mainly derived from the dissolution of carbonate rock, while the change of Mg^{2+} concentration is related to dedolomitization, and PC2 represents the water-rock interaction of carbonate rock to hydrochemistry.

(2) The cumulative total variance contribution rate of the four principal components in the direct recharge area is 86.083%, including 86.083% of the original chemical data (Table 2.). The variance contribution rate of PC1 is 29.321%, which is mainly related to Na^+, Cl^-, HCO_3^-, PH and TDS. The ion scale coefficient results show that Cl^- and NO_3^- in karst water are mainly affected by human activities. PC1 represents the influence of human activities on karst water.

Table 2. Matrix of rotated factor loadings

	Discharge area		Direct recharge area				Indirect recharge area			
	PC1	PC2	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
K^+	-0.728	0.649	-0.027	-0.897	0.043	0.011	-0.008	0.119	0.919	-0.030
Na^+	-0.433	0.857	0.835	-0.126	0.059	0.374	0.179	0.937	0.018	0.054
Ca^{2+}	0.975	-0.182	0.424	0.483	0.733	0.084	0.917	0.140	-0.247	0.004
Mg^{2+}	0.310	0.852	0.381	0.142	0.068	0.587	0.714	0.040	0.135	-0.063
Cl^-	-0.027	0.954	0.839	0.111	0.349	0.241	0.308	0.901	-0.147	-0.024
SO_4^{2-}	0.175	0.980	0.109	-0.099	0.967	0.108	0.825	0.185	-0.095	-0.359
HCO_3^-	0.943	-0.321	0.753	0.599	0.156	0.130	0.803	-0.073	-0.066	0.518
F^-	-0.440	0.653	0.041	-0.004	0.191	0.903	-0.085	-0.039	-0.012	0.696
NO_3^-	0.987	-0.054	0.011	0.610	0.422	0.460	0.726	-0.147	-0.030	-0.418
TH	0.996	-0.051	0.488	0.474	0.679	0.241	0.967	0.130	-0.178	-0.012
COD	-0.626	0.730	-0.150	-0.745	-0.179	0.000	-0.146	0.503	0.326	-0.208
PH	-0.831	0.513	-0.761	-0.101	-0.264	0.350	-0.162	-0.099	0.911	0.032
TDS	0.919	0.393	0.610	0.427	0.608	0.269	0.949	0.279	-0.120	0.037
characteristic value	8.557	5.479	4.398	3.393	3.163	1.957	6.771	2.228	1.954	1.384
Contribution rate/%	57.050	36.525	29.321	22.623	21.089	13.050	45.137	14.852	13.030	9.224
Cumulative contribution rate/%	57.050	93.575	29.321	51.944	73.033	86.083	45.137	59.989	73.018	82.243

The PC2 is composed of K^+, NO_3^-, COD, and HCO_3^-, and the variance contribution rate is 22.623%. The contribution rate of Ca^{2+} to PC2 is second only to PH, Mg^{2+} and HCO_3^-. According to the ion proportional coefficient, Ca^{2+}, Mg^{2+} and HCO_3^- in karst water are mainly derived from the dissolution of carbonate rocks, while the change of Mg^{2+} concentration is related to dedolomitization, and PC2 represents the water-rock interaction of carbonate rocks.

The PC3 variance contribution rate is 21.089%, which consists of Ca^{2+}, SO_4^{2-}, TDS and total hardness. SO_4^{2-} and Ca^{2+} are the main variables and are mainly related to the dissolution of minerals such as gypsum. Due to the high correlation between SO_4^{2-} and Ca^{2+}, TDS and total hardness, PC3 represents the influence of the dissolution of sulfate minerals on the hyrochemical composition .

The PC4 is mainly F^-, and the variance contribution rate is 13.05%, which is related to the dissolution of fluorite minerals. PC4 represents the effect of the dissolution of the fluorine-containing mineral on the hydrochemical composition.

(3) The cumulative total variance contribution rate of the four principal components in the indirect recharge area is 82.243%, which includes 82.243% of the original data (Table 2.). The variance contribution rate of PC1 is 45.137%, which is mainly related to Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^-, NO_3^-, TDS and total hardness. The ion scale coefficient results show that Cl^- and NO_3^- in karst water are mainly affected by human activities. PC1 represents the influence of human activities on karst water.

The PC2 consists of Na^+ and Cl^-, and the variance contribution rate is 14.852%. The contribution rate of Ca^{2+} to the second principal component is second only to PH, Mg^{2+} and HCO_3^-. According to the ion proportional coefficient, Ca^{2+}, Mg^{2+} and HCO_3^- ions in karst water are mainly derived from the dissolution of carbonate rock, while the change of Mg^{2+} ion concentration is related to dedolomitization, and PC2 represents the water-rock interaction of carbonate rock.

The PC3 variance contribution rate was 13.03%, which consisted of K^+ and pH. May be related to the dissolution of potassium-containing minerals such as K-feldspar. PC3 represents the effect of the dissolution of potassium-containing minerals on the chemical constituents of water.

The PC4 is mainly F^-, and the contribution rate of variance is 9.224%, which is related to the dissolution of fluorite minerals. PC4 represents the effect of the dissolution of the fluorine-containing mineral on the chemical composition of the water.

In summary, the first principal components of direct, indirect and excretory areas all represent the impact of human activities on hydrochemical components, and they account for a large proportion. Therefore, the impact of human activities on groundwater environment should not be neglected and must be paid great attention to.

5. Conclusion

In summary, the following conclusions can be obtained.

(1) The groundwater cations in the study area are dominated by Ca^{2+}, and the anions are mainly HCO_3^- and SO_4^{2-}. The type of hydrochemistry in the study area is mainly HCO_3-Ca or $HCO_3.SO_4$-Ca .

(2) The groundwater in the study area is mainly affected by the weathering of rock minerals such as carbonate, halite and sulfate,and the influence of human activities should not be ignored.

References

[1]   Wang Donghai, Li Chun, Gao Yan, Li Daqiu,Influence of human activities on groundwater quality in Jinan spring catchment,Environmental monitoring in China.19(2003)18-21.

[2]   Lu Honghai,Zhang cheng,Evolution of Karst Water Quality in Jinan spring catchment and Its Response to Human Activities.Research of Soil and Water Conservation.14(2007)236-240.

[3]   Kang, F.X., Jin, et al,Sustainable Yield of a Karst Aquifer System: A Case Study of Jinan Springs in Northern China,Hydrogeology Journal.19(2011)851-863.

[4]   Gao Zongjun, Xu Junxiang, Wang Shichen, et al,Distribution characteristics of trace elements in karst water of Jinan and its hydrogeological significance,Geoscience Frontiers. 21(2014)135-146.

[5]   Yang Lizhi, Liu Chunhua, Zhai Xiaofan.Study on the variation of hydrochemical characteristics of spring water in Jinan,Journal of water resources and water engineering.27(2016)59-64.

[6]   Zhou Juan,Study on seepage field characteristics of karst spring drainage area in Jinan,University of Jinan,Jinan, 2016.

[7]   Chi Guangyao, Xing Liting, Zhu Hengxiang, et al, Quantitative relationship between atmospheric precipitation and dynamic changes of Jinan spring, Groundwater.39 (2017)8-11.

[8]   Qin Pinrui,Numerical simulation of karst water system and water supply and exploitation scheme for protecting spring in Jinan,Water resources protection.34 (2018)30-36+103.

[9]   Chi Guangyao, Xing Liting, Hou Xinyu, et al,Dynamic study of karst springs based on wavelet analysis and Mann-Kendall method,Carsologica Sinica..37(2018) 515-526.

[10]   Zhao Zhanfeng,Ou Lu,Qin Dajun, et al.Hydrochemical characteristics and influencing factors of karst water in Jinan,China Rural Water and Hydropower.7(2012)31-37.

[11]   Wang Junyu,Wang Jiale,Jin Menggui.Hydrochemical characteristics and genesis of karst water in Jinan spring catchment.Earth Science.42(2017)821-831.

[12]   Li Qiao, Zhou Jinlong,Gao Yexin,et al,Study on hydrogeochemical characteristics in the plain area of Manas River Basin, Xinjiang,Modern geology.29(2015)238-244.

[13]   GIBBS R J,Mechanisms controlling world hydrochemistry,Science.170(1970)1088-1090.

[14]   Xing Lina,Hydrochemical characteristics and hydrogeochemical processes on typical sections of the North China Plain ,University of Geosciences in China,Beijing,2012.