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Hydrochemical Characteristics and Evolution Laws of Drinking Groundwater in Pengyang County, Ningxia, Northwest China

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Abstract: The purpose of the paper is to identify the chemical characteristics of drinking groundwater and its distribution patterns in Pengyang County and to discover the hydrochemical evolution laws of groundwater. The temporal and spatial variation of groundwater hydrochemical characteristics and evolution laws were comprehensively and systematically studied based on the understanding of the geological, hydrogeological, meteorological and hydrological conditions. Many analytical methods such as descriptive statistics, geostatistical analysis, ionic ratio coefficient method and correlation analysis were adopted based on the underground water quality analysis data. Study results showed that variation coefficients of chemical parameters of pore water in unconsolidated rocks were relatively high which indicated that water chemical compositions are vulnerable to topography, meteorology, hydrology and human activities. TDS variation was in accordance with the changes in Ca^{2+}, Mg^{2+} and SO_4^{2-} concentration. Hydrochemical type varied from $HCO_3{\cdot}SO_4$-$Na{\cdot}Ca{\cdot}Mg$ type and $HCO_3{\cdot}SO_4$-$Ca{\cdot}Mg$ type at the upper reaches towards gradually to HCO_3-Na type at the lower reaches. Ionic ratio coefficient analysis showed that the hydrodynamic conditions of the pore water in loose rocks were better than that of pore-fissure water in clastic rocks and groundwater was non-marine deposited water. Its formation effects include the weathering leaching effects of the formation containing rock salt, water-rock interaction and cation exchange reaction. Hydrochemical characteristics were mainly controlled by geological and hydrogeological conditions. Correlation analysis showed that the dissolution of rock salt and sodium sulfate salt as well as calcite precipitation occurred in pore water and in pore-crack water in clastic rocks the dissolution of albite, *K*-feldspar and the precipitation of dolomite were also important effects.

Keywords: Drinking groundwater, Groundwater, Hydrochemical characteristics, Evolution laws, Pengyang County, Correlation analysis

Introduction

Pengyang County is situated in the southern mountain area of Ningxia Hui Autonomous Region. The area is 62 km long from north to south, 58 km wide from east to west and covers 3241.1 km^2. As is located in sub-humid and semi-arid areas, the annual precipitation here is small with strong evaporation, surface water quality is poor with strong seasonality and groundwater resources are not very rich either, which together made it one of the most serious water-shortage areas in the world. Groundwater here is the main source of drinking water of local residents and the availability and quality of groundwater resources in the area have been closely related to the local economic development and people's living standards, which indicates the necessity for carrying out hydrochemical field and evolution laws research. The chemistry of groundwater is an essential parameter to assess the environmental characteristics of an area[1~2]. The main factors affecting water quality changes are lithofacies geographical conditions, groundwater recharge and runoff conditions, the opening degree of groundwater systems[3]. Through chemical characteristics research and evolution research, the chemical characteristics and its distribution pattern of drinking groundwater can be identified, the mechanism of interaction between groundwater and the environment can be revealed through groundwater chemical evolution research, and all of these are of great theoretical significance and practical significance to promote the regional socio-economic development, environmental protection and governance. In this paper, in order to provide theoretical support for the rational exploitation of groundwater, descriptive statistical analysis, geostatistical method, correlation analysis, the ionic ratio coefficients method were synthetically used to do a comprehensive and systematic study on the temporal and spatial variability of the groundwater hydrochemistry and evolution laws and to reveal the major hydrochemical evolutionary processes of groundwater quality.

Overview of the study area

Pengyang County is situated in south of Ningxia Hui Autonomous Region, east of Liupan Mountains. It is situated between longitude from 106°32'E to 106°58'E, latitude from 35°4l'N to 36°17'N (Figure 1). Typical semi-humid, semi-arid climate with four distinct seasons is dominated here, hot and rain are in the same quarter with little rain and strong evaporation. Average annual rainfall is 450 mm and the rainfall distribution is uneven in space and time, precipitation in the region mostly concentrated in July, August and September, and the total precipitation of the three months, in form of storm rain, accounted for nearly 60% of the total precipitation in the whole year. Precipitation during crop growing period accounted for only 25% of annual precipitation[4]. The average annual evaporation is 1400~1600 mm, which is three times of the rainfall. Rivers in Pengyang County including Ruhe River, Honghe River and Anjiachuan River all belong to Jinghe River system. Ruhe River and Honghe River originates from Xiaoguan Mountain while Anjiachuan River originates from "North-South Ancient spine" in northwest Pengyang. Surface water runoff is characterized by small base flow, large flood runoff, obvious seasonality and poor water quality. Landscape types in the region are dominated by medium and low mountains, loess hills and river valley terraces. The exposed rock strata are mainly Cretaceous sandstone in the western and eastern part of the stuffy area, Tertiary sandstone and muddy siltstone covered in the middle and Quaternary alluvial and proluvial deposits in the southern plain area. Based on the groundwater occurrence conditions and water features, groundwater in Pengyang can be divided into four different types including pore water in loose rocks, pore-crack water in clastic rocks, bedrock fissure water and karst fissure water in carbonate rock.

Bedrock fissure water and karst fissure water in carbonate rock have no water supply significance due to limited distribution in scope and pore water in loose rocks and pore-crack water in clastic rocks are important water supply aquifers which are rich in water resources.

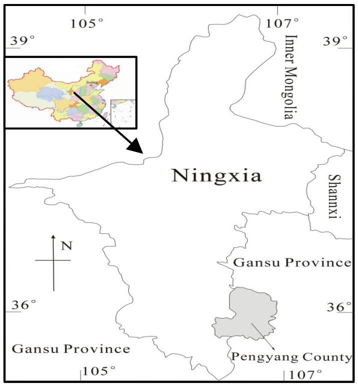

Figure 1. Location of the study area

Experimental

Descriptive statistical analysis on hydrochemical parameters is the foundation to study its characteristics and evolution laws. Through descriptive statistical analysis, we can roughly understand the enrichment and evolution laws of the chemical compositions in groundwater. A total of 74 samples buried less than 10 meters were collected across the study area and all the samples were analyzed according to the standards proposed by Chinese Ministry of Water Resources. The statistical analysis on the hydrochemical parameters of pore water in loose rocks and pore-crack water in clastic rocks in this paper was conducted with statistical software SPSS 13.0 for Windows. The calculated results are shown in Table 1.

Table 1. Descriptive statistical eigenvalue of hydrochemical parameters of different groundwater types

item	pore water in loose rocks					pore-crack water in clastic rocks				
	Min	Max	Mean	SD	Cv, %	Min	Max	Mean	SD	Cv, %
K^+	1.00	7.00	2.26	1.13	49.94	1.30	5.50	3.05	1.25	40.94
Na^+	32.00	484.00	136.89	90.70	66.25	44.60	792.00	227.96	185.68	81.45
Mg^{2+}	4.75	146.00	39.82	23.71	59.54	21.37	90.21	47.17	20.43	43.31
Ca^{2+}	11.74	195.60	44.61	31.12	69.76	27.38	78.24	42.71	17.05	39.92
Cl^-	13.81	151.89	45.45	32.87	72.32	27.62	296.87	108.74	70.72	65.04
SO_4^{2-}	10.61	1437.94	177.30	245.61	138.53	112.20	838.47	274.61	201.04	73.21
HCO_3^-	210.01	652.18	388.61	88.23	22.70	301.01	739.98	433.75	121.06	27.91
TDS	252.09	2441.07	660.59	385.12	58.30	463.61	2414.01	943.26	497.90	52.78
NO_3^-	0.00	20.32	4.13	4.20	101.69	0.00	22.58	4.78	6.13	128.28
TH	91.77	900.18	253.15	147.30	58.19	153.36	399.72	269.62	84.83	31.46
pH	7.74	8.36	8.11	0.11	1.37	7.89	8.34	8.09	0.10	1.30

Note: Units in the column are mg/L except pH. SD for Standard deviation, Cv for Coefficient of variation

Results and Discussion

The variation trends of major ion are basically the same in both pore water in loose rocks and pore-crack water in clastic rocks. The anion and cation with biggest concentrations are HCO_3^- and Na^+ respectively and the smallest are Cl^- and K^+ respectively. Hydrochemical types are mostly compound water of anions HCO_3^-, SO_4^{2-} with the cations Na^+, Mg^{2+} and Ca^{2+}. pH values are higher than 7 which indicates that groundwater is alkaline and the variation coefficient of pH is relatively small which indicates that the spatial variation of pH in groundwater is weak and the occurrence conditions of groundwater has weak effects on the spatial variation of pH.

All the variation coefficients of the hydrochemical parameters in pore water except Na^+ and NO_3^- are bigger than those in pore-crack water. This shows that the spatial variability of hydrochemical properties of the pore water in loose rocks is stronger than that of pore-crack water in the clastic rocks, being vulnerable to external factors such as topography, hydro-meteorology and human activities due to its smaller buried depth.

In the pore water of loose rocks, the variation coefficient of HCO_3^- is relatively smaller, indicating weaker spatial variability of HCO_3^- and relative stability in its content. Whereas SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Na^+, Mg^{2+} and K^+ possess bigger variation coefficients, which reflects the existence of a strong spatial variability in their contents. At the same time, SO_4^{2-}, Na^+ and HCO_3^- show bigger mean values and bigger standard deviations, which indicate that the absolute contents of these three ions in pore water of loose rocks are higher and are the major constituents of groundwater that determine the hydrochemical groundwater types. The variation coefficients of major ions in the pore-crack water of clastic rocks are relatively smaller, which indicates the contents in groundwater are less affected by outside interference.

Spatial variations of TDS, TH and hydrochemical types

The spatial variation characteristics of TDS and TH

TDS and TH are important indicators to evaluate groundwater quality. TDS is usually affected by topography, lithology, burial conditions, groundwater recharge, runoff and discharge conditions as well as human activities. According to the level of TDS, groundwater can be divided into fresh groundwater (TDS<1000 mg/L), moderately salty water (1000<TDS<3000 mg/L) and salty water (TDS>3000 mg/L) and according to the grading standards of TH (as $CaCO_3$), groundwater can be divided into soft water (TH<150 mg/L), moderately hard water (150<TH<300 mg/L), hard water (300<TH<450 mg/L), extremely hard water (TH>450 mg/L). TDS and TH contours maps are drawn with the Surfer 9 software with application of the theory and methods of geostatistics and Kriging interpolation method (Figure 2 & 3).

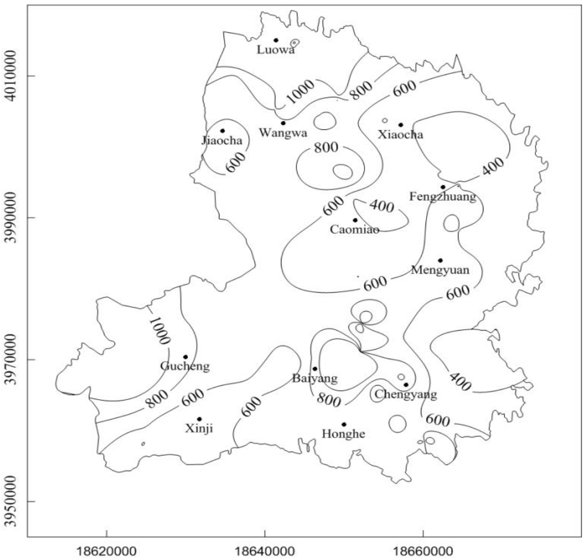

Figure 2. Contours map of TDS in Pengyang drinking groundwater

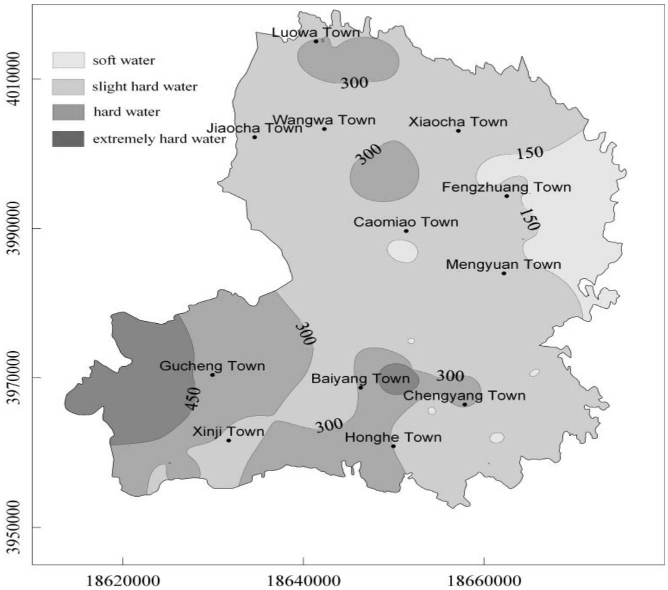

Figure 3. Zoning map of TH in Pengyang drinking groundwater

From Figure 2 we can see that in most parts of the study area the groundwater is fresh water with TDS<1000 mg/L which is suitable for human and animal consumption. Only around northern Luowa Town and the vicinity of the southwestern Gucheng Town, TDS varies from 1000 to 3000 mg/L, being moderately salty water. And salty water does not appear in the study area. TDS generally shows a gradual decrease trend from west to east. Of the total 74 groundwater samples collected during the research, the fresh water samples accounted for 83.78%, moderately salty water samples accounted for 16.22%. By analysis on the concentrations of major ions, concentrations of Ca^{2+}, Mg^{2+} and SO_4^{2-} show similar changes with the TDS, which can help us to conclude that the change of TDS is determined by the concentrations of Ca^{2+}, Mg^{2+} and SO_4^{2-}.

From Figure 3 we can see that the TH of groundwater in the study area is generally large. The groundwater in study area except in Fengzhuang Town and the eastern part of Mengyuan Town is moderately hard water, hard water and extremely hard water. Extremely hard water is mainly distributed in the western of Gucheng Town and the eastern regions of Pengyang County in small-scale whereas moderately hard water and hard water are found in the central and southern parts in larger-scale distribution. The TH shows a gradual decrease trend from west to east, which shows that in western part of the study area, the contents of Ca^{2+} and Mg^{2+} are relatively larger, as the groundwater runs downstream, contents of Ca^{2+} and Mg^{2+} decline. The trend of TH shows good consistency with TDS, which further illustrates that Ca^{2+} and Mg^{2+} are the main factors affecting the changes in TDS.

Spatial evolution laws of hydrochemical types

Regional hydrochemical characteristics are usually determined by the constant components in groundwater. The hydrochemical types are classified in accordance with internationally accepted classification standards. The analyzing processes are as follows: Firstly, the millinormal percentage of the ions is calculated, if its value is higher than 25%, it can be considered as the main ions involved in hydrochemical classification. Then Kriging spatial interpolation method will be adopted to draw the cation and anion hydrochemical type partition map respectively. After comprehensive analysis we can obtain the distributions of hydrochemical types. Hydrochemical map of cation and anion are shown in Figure 4 and Figure 5, respectively:

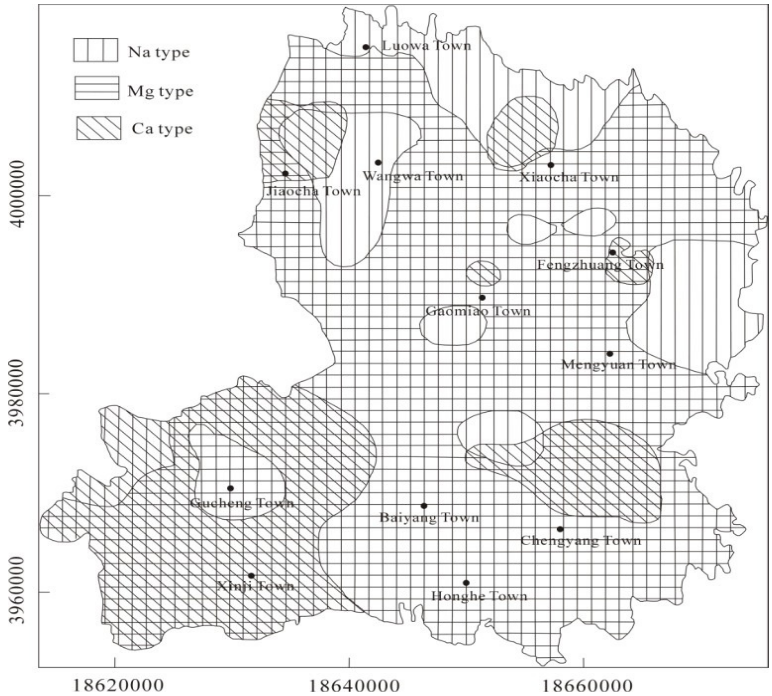

Figure 4. Hydrochemical types of cations in the study area

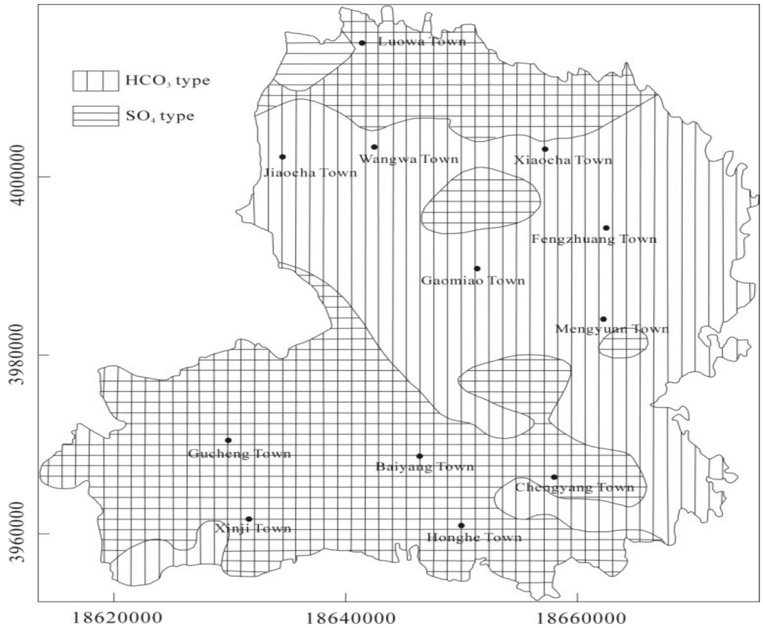

Figure 5. Hydrochemical types of anions in the study area

It can be seen from Figure 4 that Na-type water distributes across the whole study area. What makes the difference is that different cations superimpose in different regions. For example, around Gucheng Town, Xinji Town and Chengyang Town, Na-type water is superimposed with Mg-type water and Ca-type water, forming Na·Ca·Mg compound water, and around the intersection of Xiaocha Town, Jiaocha Town and Wangwa Town, Na-type water is superimposed with Ca-type water, forming Na·Ca compound water. In other regions Mg-type water is superimposed on, Na·Mg compound water is therefore formed. It can be seen from Figure 5 that the HCO_3 type water almost covers the whole study area and in the northern part and southwestern part of the study area HCO_3^- and SO_4^{2-} are superimposed and form $HCO_3 \cdot SO_4$ type compound water.

The above analysis results show that from southwest to northeast the content of Na^+ increases whereas Mg^{2+} and Ca^{2+} decrease. The concentration of HCO_3^- increases from north and south to the center, while the concentration of SO_4^{2-} decreases. Summarized from the above analysis, hydrochemical types of the drinking groundwater can be determined. In the southwest area $HCO_3 \cdot SO_4$-Na·Mg·Ca type water is dominated and $HCO_3 \cdot SO_4$-Na·Mg type water is mainly distributed in the southwest of Pengyang County, while the central part is covered mainly by HCO_3-Na·Mg type water and in the northern part $HCO_3 \cdot SO_4$-Na·Mg type water and HCO_3-Na type water are widely distributed.

Ionic ratio coefficients

Hydrogeochemical evolutions of groundwater are controlled by many factors and the application of various ionic ratio coefficients is an effective means to study the material sources of groundwater evolution[5]. The various ratio coefficients of the chemical compositions in the groundwater are often used to study some hydrogeochemical problems[6~8]. Ionic ratio coefficients can reflect the hydrogeochemical environment of the water formation and water-rock interaction[9]. Ratio coefficients can help us to understand the source and the formation of groundwater compositions and can be better used to describe and depict the evolution and characteristics of water quality than the traditional single-analysis method both in time and space scale, as well as can help us to make typical analysis on hydrogeochemical evolution[8].

$\gamma Cl^-/\gamma Ca^{2+}$ coefficient

The parameter of $\gamma Cl^-/\gamma Ca^{2+}$, ratio of concentration of Cl^- and Ca^{2+} in milligram equivalent, is a parameter charactering the hydrodynamics[8] and its value can be representative of groundwater hydrodynamic conditions[10]. The higher the value is, the worse the hydrodynamic conditions. Parameter of $\gamma Cl^-/\gamma Ca^{2+}$ in pore water and pore-crack water are 0.57 and 1.43, respectively. This shows that hydrodynamic conditions in the pore water of loose rocks are better than that in pore-crack water of clastic rocks. Usually, Ca^{2+} is a dominant cation in a low-mineralized environment. With the TDS increasing, Mg^{2+} will gradually increase. With the TDS further increasing, Na^+ in groundwater will become the dominant cation[10]. The worse the hydrodynamic conditions, usually the higher the TDS is, and when TDS is high, Cl^- is hard to migrates, and the concentration of Cl^- will increase with TDS. At the same time, Ca^{2+} will decline with TDS, which finally will cause the parameter of γCl-/γCa^{2+} to be relatively higher. On the contrary, when runoff conditions are good, the parameter of γCl-/γCa^{2+} will be relatively lower.

$\gamma Na^+/\gamma Cl^-$ coefficient

The ratio of $\gamma Na^+/\gamma Cl^-$ is a hydrogeochemical parameter characterizing the concentration level of Na^+ in groundwater. The average $\gamma Na^+/\gamma Cl^-$ coefficient value of standard seawater is 0.85, low-mineralized water has a higher $\gamma Na^+/\gamma Cl^-$ coefficient ($\gamma Na^+/\gamma Cl^->0.85$) and highmineralized water has a lower $\gamma Na^+/\gamma Cl^-$ coefficient ($\gamma Na^+/\gamma Cl^-<0.85$)[6~8]. Relationship of γNa^+ and γCl^- in the study area is shown in figure 6. As can be seen from Figure 6, all water samples are located above 1:1 line, which indicates the concentration of Na^+ in milligram equivalent is greater than that of Cl^-, that is $\gamma Na^+/\gamma Cl^->1$, which shows that groundwater in the area is non-marine deposited water[11~12], its chemical composition is not only the results of weathering-leaching effect of formations containing rock salt, but also the results of water-rock interaction and the exchange reaction of Ca^{2+} in the groundwater with Na^+ in solid soil particles.

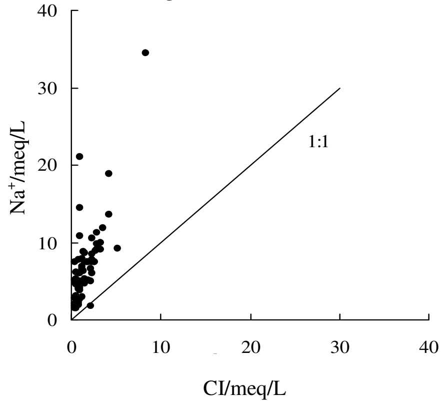

Figure 6. Relationship of γNa^+ and γCl^- in the study area

The discussion and analysis of these ionic ratio coefficients show that the overall hydrochemical characteristics of the study area are mainly controlled by geological and hydrogeological conditions. Hydrodynamic conditions greatly affect the groundwater chemical compositions and hydrochemical changes.

Ionic correlation analyses

Correlation analysis can reveal the similarity of groundwater chemical parameters and consistency and differentiation of sources of groundwater[7]. Statistical software SPSS 13.0 for Windows was adopted to calculate the Pearson correlation coefficients and the calculated results are listed in Table 2.

In pore water of loose rocks, Na^+, Mg^{2+} and SO_4^{2-} has a significant positive correlation with TDS, and their correlations have passed significance test at the 0.01 level and correlation coefficients exceed 0.8. Especially, correlation coefficient of SO_4^{2-} with TDS is 0.963. In addition, the correlations of Na^+ with $SO_4^{2-}$and Cl^- are also significant, of which the correlations have also passed significance test at the 0.01 level, from which it can be judged that during the runoff process to the downstream, from west to east, NaCl and Na_2SO_4 continuously dissolves, which leads to the increase of Na^+, $Cl^-$and SO_4^{2-}, namely:

$$NaCl=Na^++Cl^- \qquad Na_2SO_4=2Na^{2+}+SO_4^{2-} \tag{1}$$

The calculated results show that Ca^{2+} shows a negative correlation with HCO_3^- and is weakly related with TDS, which indicates that as the TDS increases, Ca^{2+} and HCO_3^- generate calcium carbonate[6~8, 13], namely:

$$Ca^{2+}+2HCO_3^-\rightarrow CaCO_3\downarrow+CO_2\uparrow+H_2O \tag{2}$$

Mg^{2+} shows a good correlation with TDS and the correlation coefficient exceeds 0.8.

Although the correlation between Mg^{2+} and HCO_3^- is not strong, a negative correlation doesn't occur, which indicates that precipitation effect of Mg^{2+} and HCO_3^- does not occur.

Table 2. Pearson correlation coefficients of hydrochemical parameters

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	TDS	TH	pH
Pore water in loose rocks										
Na^+	1.000	0.097	0.570**	0.131	0.609**	0.756**	0.533**	0.877**	0.357**	-0.563**
K^+		1.000	0.244	0.375**	0.253*	0.271$_{*}$	-0.126	0.257*	0.355**	-0.185
Mg^{2+}			1.000	0.597**	0.414**	0.841**	0.159	0.838**	0.861**	-0.604**
Ca^{2+}				1.000	0.079	0.658**	-0.233	0.553**	0.922**	-0.520**
Cl^-					1.000	0.341**	0.411**	0.526**	0.248	-0.271*
SO_4^{2-}						1.000	0.078	0.963**	0.822**	-0.753**
HCO_3^-							1.000	0.309*	-0.071	-0.038
TDS								1.000	0.754**	-0.720**
TH									1.000	-0.621**
pH										1.000
Pore-crack water in clastic rocks										
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	TDS	TH	pH
Na^+	1.000	0.220	-0.308	-0.050	0.904**	0.905**	0.860$_{**}$	0.971**	-0.253	-0.552
K^+		1.000	0.198	0.482	0.333	0.410	0.051	0.329	0.434	-0.375
Mg^{2+}			1.000	0.132	-0.242	0.019	-0.073	-0.114	0.802$_{**}$	-0.188
Ca^{2+}				1.000	0.230	0.236	-0.336	0.107	0.698$_{*}$	-0.432
Cl^-					1.000	0.871**	0.649$_{*}$	0.921**	-0.037	-0.588
SO_4^{2-}						1.000	0.738**	0.976**	0.156	-0.740
HCO_3^-							1.000	0.827**	-0.255	-0.443
TDS								1.000	-0.018	-0.668*
TH									1.000	-0.397
pH										1.000

Note: ** Correlation is significant at the 0.01 level: * Correlation is significant at the 0.05 level

In pore-crack water of clastic rocks, correlations between Na^+, Cl^-, SO_4^{2-}, HCO_3^- and TDS are significant, the correlations have passed significance test at the 0.01 level, and the correlation coefficients of Na^+, Cl^-, SO_4^{2-} with TDS exceed 0.9, correlation coefficient of HCO_3^- with TDS is greater than 0.8, whereas the correlation coefficient of K^+ with TDS is relatively lower, which indicates that Na^+, Cl^-, SO_4^{2-}, HCO_3^- increase with the TDS, whereas K^+ doesn't. In addition, the correlations of Na^+ with SO_4^{2-}, Cl^- and HCO_3- are also significant. From the increasing trend of Na^+ with Cl^- and HCO_3^-, it can be determined that during the runoff process to the downstream in pore-crack water, NaCl and Na_2SO_4 continuously dissolves and at the same time, CO_2 dissolved in the water accelerates the weathering leaching effects, leading to the dissolution of albite and K-feldspar and the generation of kaolinite. Namely:

$$NaCl=Na^++Cl^- \qquad Na_2SO_4=2Na^{2+}+SO_4^{2-} \tag{3}$$

$$4NaAlSi_3O_8+4CO_2+22H_2O=Al_4(Si_4O_{10})(OH)_8+8H_4SiO_4+4Na^++4HCO_3^- \tag{4}$$

$$4KAlSi_3O_8+4CO_2+22H_2O=Al_4(Si_4O_{10})(OH)_8+8H_4SiO_4+4K^++4HCO_3^- \tag{5}$$

At the same time, the correlations of Mg^{2+} and Ca^{2+} with HCO_3^- are negative and have weak correlation with TDS. The main reason for this phenomenon is that as the groundwater runoff downstream, the pH and TDS increase. When pH>7.4 and TDS> 600 mg/L, Ca^{2+} and HCO_3^-generates calcium carbonate precipitation[6~8], namely:

$$Ca^{2+}+2HCO_3^-\rightarrow CaCO_3\downarrow+CO_2\uparrow+H_2O \tag{6}$$

With the alkalinity increases, calcium carbonate in turn promotes the precipitation of dolomite:

$$Mg^{2+}+2HCO_3^-+CaCO_3\rightarrow CaMg\ (CO_3)_2\downarrow+CO_2\uparrow+H_2O \tag{7}$$

Reduction in Ca^{2+} makes the ratio of Mg^{2+}/Ca^{2+} increase. When the ratio of Mg^{2+}/Ca^{2+} exceeds 6, $CaCO_3$ will be transformed into CaMg $(CO3)_2$ [6], namely:

$$2CaCO_3+Mg^{2+}\rightarrow CaMg\ (CO_3)_2+Ca^{2+} \tag{8}$$

We can see from the above ionic correlation analysis that dissolution of rock salt and sodium sulfate salt and calcite precipitation have taken place both in pore water of loose rocks and in pore-crack water of clastic rocks during the flow. Particularly in pore-crack water of clastic rocks dissolution of albite and *K*-feldspar and dolomite precipitation also occurred, which can be attributed to the different sedimentary environment and different hydrogeological conditions between loose rocks and clastic rocks.

Conclusion

Hydrochemical characteristics and the evolution of drinking groundwater in Pengyang County were studied with descriptive statistical analysis, ionic ratio analysis and correlation coefficient analysis and the spatial distribution of hydrochemistry parameters was also studied with the statistical theory and method. Finally the following conclusions were obtained:

The descriptive statistical analytical results showed that the concentrations of $HCO_3^-$and Na^+ for anion and cation respectively in the drinking groundwater were the biggest and hydrochemical types were mostly compound water of the anions HCO_3^-, SO_4^{2-} and the cations Na^+, Mg^{2+}, Ca^{2+}. All pH values are higher than 7, of which the variation coefficient was relatively small, which indicated that groundwater occurrence conditions had few effects on the spatial variation of pH and groundwater chemistry. The variation coefficient values of hydrochemical parameters in pore water of loose rocks were higher than that in the pore-crack water of clastic rocks, which indicated that pore water in loose rocks were vulnerable to topography, hydrometeorology and human activities.

The spatial variations of TDS, TH and hydrochemical types were studied with geostatistical methods and the results indicated that TDS and TH showed a similar change law in the study area, namely, TDS and TH decreased gradually from west to east in the study area. TDS changes were mainly affected by the concentration change of Ca^{2+}, Mg^{2+} and SO_4^{2-}. From upstream to downstream, from west to east, the concentrations of Na^+ and HCO_3^- gradually increased and the concentrations of Ca^{2+}, Mg^{2+} and SO_4^{2-} decreased gradually. Hydrochemical type varied gradually from $HCO_3{\cdot}SO_4$-Na·Ca·Mg type water in the upper reaches to $HCO_3{\cdot}SO_4$-Ca·Mg type water in the middle reaches and to the HCO_3-Na type water in the lower reaches of the study area.

Ionic ratio coefficient analysis showed that the hydrodynamic conditions of the pore water in loose rocks were better than that of pore-crack water in clastic rocks and groundwater was non-marine deposited water. Its formation effects include the weathering leaching effects of the formation containing rock salt, water-rock interaction and the exchange reaction of Ca^{2+} in the groundwater with Na^+ in solid soil particles. Hydrochemical characteristics were mainly controlled by geological and hydrogeological conditions. The groundwater chemical composition and hydrochemical evolution were greatly affected by hydrodynamic conditions.

The correlation analysis results showed that the dissolution of rock salt and sodium sulfate salt as well as calcite precipitation occurred in both pore water of loose rocks and pore-crack water of clastic rocks. Besides, albite, *K*-feldspar dissolution and dolomite precipitation also occurred in clastic rocks.

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