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Hydrochemical characteristics of groundwater in Tongchuan City, China

Zhang Yuxi, Zhang Yuanjing* and Liu Jingtao

The Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang 050061, China.

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In order to reveal the formation mechanism of hydrochemical characteristics in Tongchuan City, we collected and detected 39 samples of underground water. Correlation analytical method, hydrochemical method and ion ratio coefficient method were employed to investigate the hydrochemical characteristics, influencing factors and principles of changing. Results demonstrate that the main factors, controlling the shallow water salinization, are the SO_4^{2-} , NO_3^- , Cl^- and K^+ . The contents of SO_4^{2-} , NO_3^- and Cl^- are greatly different and other indexes are relatively stable. The values of $\gamma\text{Na}/\gamma\text{Cl}$ demonstrate that the Na^+ is released from the soil aquifer in the runoff process. There is an exchange between the Ca^{2+} in water and Na^+ in soil, which leads to $\gamma\text{Na} > \gamma\text{Cl}$. As the exchange time in deep water is longer than that of shallow water, the exchange and adsorption of ions are more sufficient. The value of $\gamma\text{Na}/(\gamma\text{Na} + \gamma\text{Cl})$ demonstrates that with increasing of ground water depth, the level of cation exchange enhances, which leads to the dominant cation turning to Ca^{2+} from Na^+ . The value of $\gamma\text{HCO}_3 + \gamma\text{SO}_4 / \gamma\text{Ca} + \gamma\text{Mg}$ demonstrates the shallow water is mainly from atmospheric rainfall and the influence of cation exchange is more obvious on deep water. The types of shallow water in Tongchuan City are mainly $\text{HCO}_3\text{-SO}_4\text{-Ca}$. Its classification is relatively complex. Whereas, the deep water is mainly $\text{HCO}_3\text{-Na}$ and the category of underground water is simple. As for shallow water, the content of alkaline earth metal is larger than that of alkali metal. For the deep water, the content of weak acid group is larger than that of strong acid group. In the region of upper reaches, the features of both shallow and deep waters are mainly weak acid and alkaline earth metal. The chemical composition mainly consists of carbonate leaching. With the flowing of underground water, the shallow water turns to be strong acid and alkaline earth metal and the deep water turns to be weak acid and alkali metal.

Key words: Tongchuan City, underground water, hydrochemical characteristics, ion ratio coefficient method.

INTRODUCTION

The composition and distribution of hydrochemistry are direct proofs to study the formation and change of underground water. They are basic principles for exploitation and planning. The composition and

concentration distribution of hydrochemistry are formed in the development of geological history. Some geochemical conditions play important roles in the process of formation, such as the topographical distribution, meteorological and

*Corresponding author. Email: kobzhang@qq.com

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hydrological changes, geological structures, changes of hydrological conditions and human activities. Through hydrochemical information, we can explore the features of occurrence environment, runoff channels and material exchanges, which can help us to reveal the cycle principles of underground water (Florian, 2011; Ravikumar et al., 2010).

Tongchuan City is an industrial city with plenty of coal mines. Its coal and building-material industries are highly developed. So it is an important industrial base for energy and raw materials in northwest of China. In the process of development, there are large populations settled down. What is more, the scales of industry and agriculture, commerce and tourism have increased rapidly. These changes have propelled a high demand for underground water. However, the underground water has been seriously destroyed, which has affected the living water, industrial water and agricultural water. The study of underground water hydrochemistry is the main contents of water resources quality evaluation, which has an important meaning in water resources utilization and management together with the protection of the ecological environment.

In this paper, we collected underground water with the principle of scientific system. Then, relative hydrogeochemical parameters were studied. Descriptive statistics, correlation analysis, ion ratio coefficient method and Piper diagrammatic method were employed to study the characteristics of spatial and temporal variability together with the evolution rules. We also revealed the hydrochemical procedure of underground water quality evolution, which provides scientific proof for water resources protection and rational development.

MATERIALS AND METHODS

Overview of the research area

Tongchuan City is located in the transitional zone of Guanzhong Plain to loess plateau of Shanxi Province (E108°34'~109°29', N34°50'~35°34'), with an area of 3882 km². Tongchuan City has a warm temperate continental climate, which is dry and cold in winter and with scarce rain and snow. Affected by the warm moist air mass of Pacific Ocean, it is hot and humid with relative abundant rain in the summer. There are usually droughts in spring and water-logging in autumn. The topography of Tongchuan City is north-west high and south-east low, which results in the obvious difference of climate. The average precipitation is 555.8~709.3 mm and the average temperature is 8.9~12.3°C.

Collection and analysis of samples

In August 2011, we collected 39 samples of underground water in Tongchuan City, which consists of 25 groups of shallow water (well total depth less than 30 m) and 14 groups of deep water (well total depth more than 100 m), which are shown in Figure 1. The parameters to be detected include HCO₃⁻, SO₄²⁻, NO₃⁻, Cl⁻, Ca²⁺, Na⁺, Mg²⁺, K⁺ and total dissolved solids (TDS). The detection of samples was carried out in underground mineral water and

environmental monitoring center of the Ministry of Land and Resources. The equipments used are as follows: flame atomic absorption spectrophotometry was employed to detect the concentration of K⁺ and Na⁺; Ion chromatography was used to detect SO₄²⁻ and Cl⁻; ethylenediaminetetraacetic acid (EDTA) titrimetry was used to study HCO₃⁻; Gas phase molecular absorption spectrometry was used to detect NO₃⁻; The value of TDS is the sum of ion concentration; we use SPSS18.0 and AquaChem3.7 were used to analyze the data.

RESULTS AND DISCUSSION

Descriptive statistics

The negative ions of underground water in Tongchuan City mainly consist of HCO₃⁻, SO₄²⁻, NO₃⁻ and Cl⁻ (as shown in Table 1). Especially, the concentration of HCO₃⁻ is the most high (in the range from 213 to 621.7 mg/L), with an average value of 353.11 mg/L. The contents of other ions are as follows: SO₄²⁻ (in the range from 13.18 to 897 mg/L) has an average value of 221.95 mg/L; NO₃⁻ (in the range from 6.98 to 482.5 mg/L) has an average value of 96.61 mg/L; Cl⁻ (in the range from 5.25 to 208.3 mg/L) has an average value of 53.06 mg/L. The positive ions of underground water mainly consist of Ca²⁺, Na⁺, Mg²⁺ and K⁺. Especially, the concentration of Ca²⁺ is most high (in the range from 12.71 to 457.2 mg/L), with an average value of 129.32 mg/L. The contents of other ions are as follows: Mg²⁺ (in the range from 15.64 to 126.5 mg/L) has an average value of 42.99 mg/L; K⁺ (in the range from 0.31 ~ 31.6 mg/L) has an average value of 3.21 mg/L. The value of TDS is in the range between 305.8 and 2343 mg/L, with an average value of 821.59 mg/L. For all the samples, 71.79% are fresh water and 28.21% belong to the brackish water. From the variation coefficients of components, we can conclude that NO₃⁻ has the highest variation coefficients in negative ions, which suggests that there is a large distribution in the contents of NO₃⁻. There are also a large variation in the contents of SO₄²⁻ and Cl⁻. However, the variation coefficient of HCO₃⁻ is the smallest, which suggests that its content is relative stable. In the four positive ions, K⁺ has the highest variation coefficient, which suggests it has a wider distribution difference than others. The changing degree of negative ions is larger than that of positive ions.

There are some differences between the hydrochemical characteristics of shallow water and deep water. As for the negative ions, the concentration of HCO₃⁻ and NO₃⁻ show no obvious difference between the shallow water and deep water; the concentrations of SO₄²⁻ and Cl⁻ are 3 and 2 times higher than that of deep water respectively. Compared with deep water; the proportions of HCO₃⁻ and NO₃⁻ in negative ions are lower and the proportions of SO₄²⁻ and Cl⁻ are higher. As for positive ions, the average contents of Ca²⁺, Mg²⁺ and K⁺ are all higher than that of deep water. However, the concentration of Na⁺ is lower than deep water. Ca²⁺ possess the maximum percentage

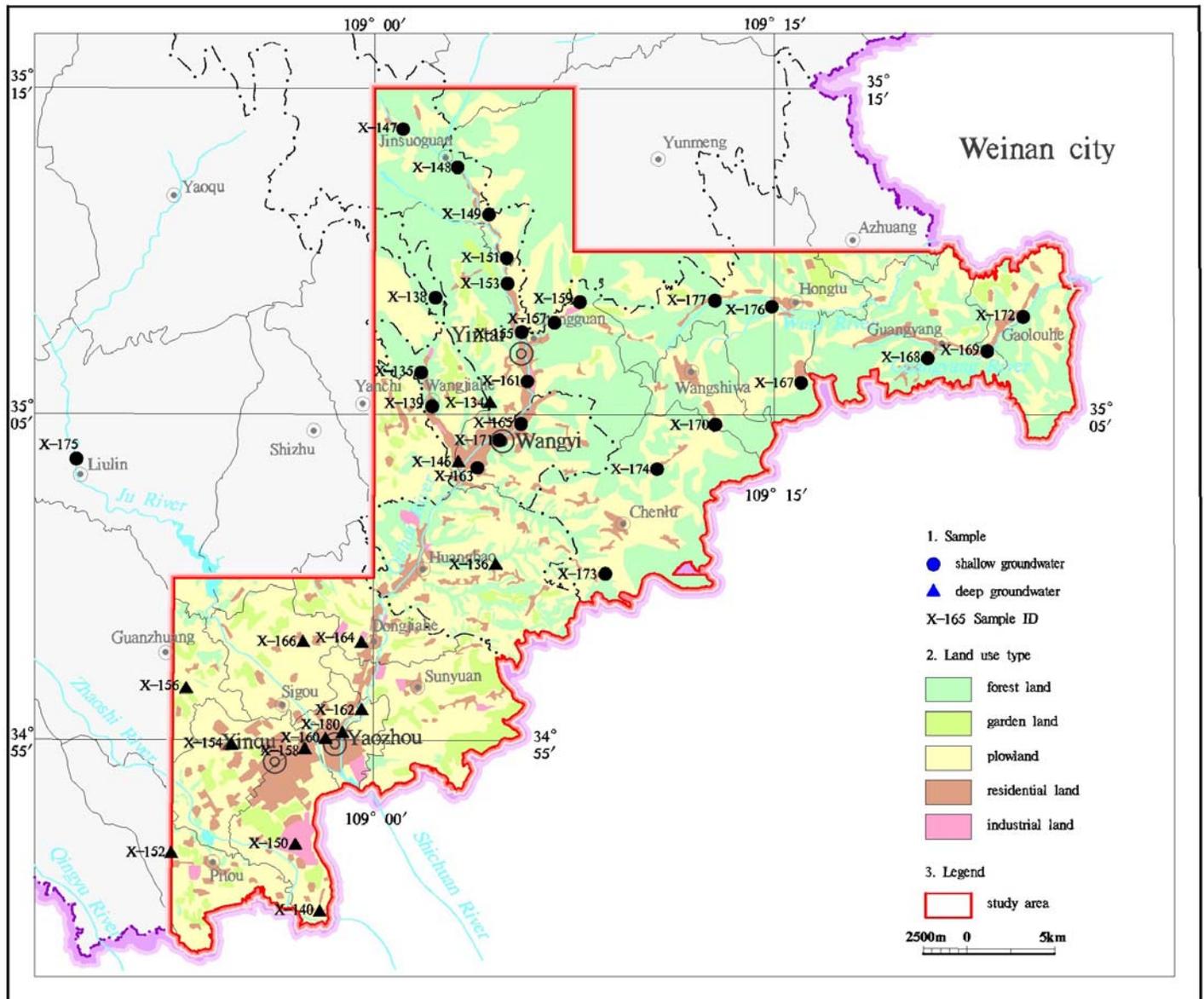


Figure 1. Location and detailed land use regionalization of the study area [groundwater sampling sites are shown as triangles (deep groundwater) and circles (shallow groundwater)].

in shallow water, which is 54.86% and Na^+ is the maximum one in deep water, which is 55.47%. What is more, the average value of TDS in shallow water is 1 times more than that of deep water, which suggests that there is a high ion content in the shallow water.

Generally, the ion variation coefficient of shallow water is higher than that of deep water. Among them, K^+ has the biggest change, which suggests that there is a more obvious variation in shallow water than that in deep water. This is caused by the aquifer medium, topography, hydrology-weather conditions and human activities. There shallow water, which demonstrates that they have relatively stable features. Among them, HCO_3^- has a smaller variation for HCO_3^- , Ca^{2+} , Na^+ and Mg^{2+} in

maximum average value, with a minimum variation coefficient, which suggests that it has a higher relative contents and it is the main negative ions. There are higher variation coefficients in SO_4^{2-} , NO_3^- , Cl^- and K^+ , which suggests they are sensitive to the change of environment, with bigger change in shallow water. In deep water, there are bigger variation coefficient in SO_4^{2-} , NO_3^- and Cl^- . We can conclude that they have a bigger contents change and a smaller variation in shallow water.

Correlation statistics

Correlation statistics can be used to reveal the similarity,

Table 1. Summary statistics of the analytical data and groundwater samples of the study area.

Groundwater samples	Statistical evaluation	Unit	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Ca ²⁺	Na ⁺	Mg ²⁺	K ⁺	TDS
All samples	Min	mg/L	213	13.18	6.98	5.25	12.71	19.02	15.64	0.31	305.8
	Max	mg/L	621.7	897	482.5	208.3	457.2	205.7	126.5	31.6	2343
	Mean	mg/L	353.11	221.95	96.61	53.06	129.32	79.24	42.99	3.21	821.59
	S.D	mg/L	76.8	226.45	116.77	51.73	96.8	43.04	27.16	5.87	448.24
	C.V	%	21.75	102.03	120.86	97.5	74.85	54.31	63.17	183.02	59.43
Shallow groundwater	Min	mg/L	224.5	21.19	9.8	5.25	24.31	19.02	20.12	0.31	305.8
	Max	mg/L	488.1	854.7	482.5	208.3	331.6	155.8	126.5	31.6	1944
	Mean	mg/L	355.2	266.02	92.69	63.31	153.94	72.07	50.38	4.21	924.92
	S.D	mg/L	67.68	223.04	119.4	55.51	81.86	41.24	30.07	7.27	458.72
	C.V	%	19.05	83.84	128.81	87.68	53.18	57.22	59.69	172.85	49.6
Deep groundwater	Min	mg/L	279.2	13.18	9.3	5.25	12.71	50.24	15.64	0.77	354.4
	Max	mg/L	621.7	185.5	364	64.77	90.26	205.7	41.56	1.71	695.7
	Mean	mg/L	369.56	63.48	106.47	23.14	48.5	95.29	26.78	1.22	491.3
	S.D	mg/L	96.46	49.13	128.54	18.36	24.04	46.11	9.74	0.29	119.74
	C.V	%	26.1	77.39	120.73	79.33	49.56	48.38	36.38	23.6	24.37

S.D: Standard deviation; C.V: coefficient of variation.

Table 2. Correlation matrices of hydrochemical parameters of groundwater in the study area.

Parameters	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Ca ²⁺	Na ⁺	Mg ²⁺	K ⁺	TDS
Shallow groundwater	HCO ₃ ⁻	1							
	SO ₄ ²⁻	-0.07	1						
	NO ₃ ⁻	-0.06	0.22	1					
	Cl ⁻	0.05	0.57 ^b	0.16	1				
	Ca ²⁺	-0.09	0.92 ^b	0.2	0.67 ^b	1			
	Na ⁺	0.46 ^a	0.25	0.19	0.63 ^b	0.16	1		
	Mg ²⁺	0.13	0.84 ^b	0.09	0.82 ^b	0.78 ^b	0.53 ^b	1	
	K ⁺	-0.07	0.11	0.57 ^b	0.27	0.18	0.17	0.08	1
	TDS	0.07	0.89 ^b	0.22	0.86 ^b	0.91 ^b	0.53 ^b	0.93 ^b	0.23
Deep groundwater	HCO ₃ ⁻	1							
	SO ₄ ²⁻	-0.19	1						
	NO ₃ ⁻	0.03	-0.15	1					
	Cl ⁻	-0.35	0.97 ^b	-0.12	1				
	Ca ²⁺	-0.44	0.72 ^a	0.21	0.75 ^b	1			
	Na ⁺	0.86 ^b	-0.11	-0.29	-0.25	-0.65 ^a	1		
	Mg ²⁺	0.28	0.71 ^a	0.15	0.67 ^a	0.46	0.2	1	
	K ⁺	0.15	0.47	0.07	0.38	0.55	-0.06	0.48	1
	TDS	0.56	0.68 ^a	-0.11	0.56	0.23	0.56	0.87 ^b	0.48

a p<0.05; b p<0.01.

dissimilarity, consistency and difference of underground water hydrochemical characteristics (Kshetrimayum and Bajpai, 2012). The Pearson correlation coefficients of shallow and deep waters in Tongchuan City are

calculated as shown in Table 2. In shallow water, there is strong positive correlation between TDS and SO₄²⁻, Cl⁻, Ca²⁺, Na⁺ and Mg²⁺. However, HCO₃⁻, NO₃⁻ and K⁺ have no effects on TDS. Above results demonstrate that TDS is

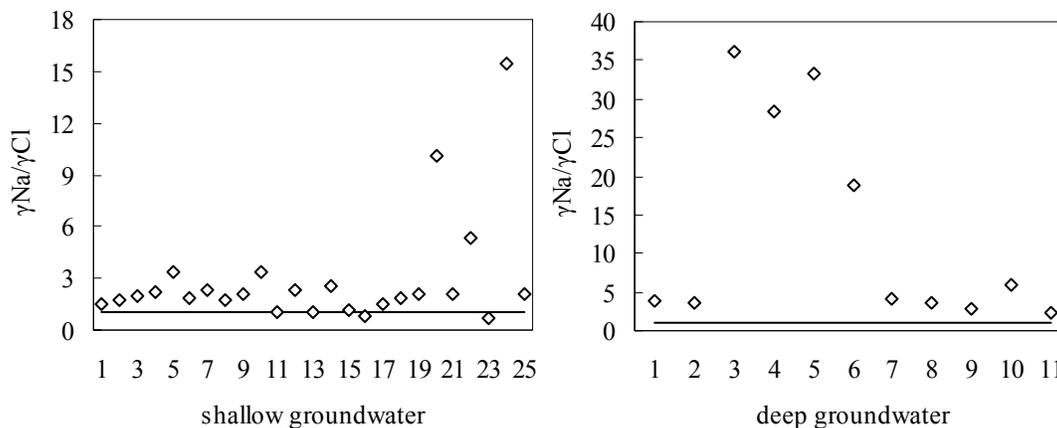


Figure 2. Scattergram of γ_{Na}/γ_{Cl} values of groundwater.

mainly controlled by SO_4^{2-} , Cl^- , Ca^{2+} , Na^+ and Mg^{2+} . There are perfect positive correlations between Ca^{2+} , Mg^{2+} and SO_4^{2-} , Cl^- , which suggests that Ca^{2+} and Mg^{2+} are mainly from sulfate and chlorate. There is a strong positive correlation between Na^+ and Cl^- , which suggests that Na^+ and Cl^- are mainly from chlorate. There is also positive correlation between K^+ and NO_3^- , which demonstrates that they are from the same source (Dudeja et al., 2011). There is a strong positive correlation between TDS and Mg^{2+} and it also has some relationships with SO_4^{2-} . The effects of other indexes are relatively slight. All of the above results demonstrate that in the deep water TDS is mainly controlled by Mg^{2+} and SO_4^{2-} . Consistent with shallow water, there are perfect positive correlations between Ca^{2+} , Mg^{2+} and SO_4^{2-} , Cl^- in deep water. Different from shallow water, there is no positive correlation between Na^+ and Cl^- . There is also no relationship between K^+ and other ions in deep water.

Analysis of ion ratio coefficient

In the flow field of underground water, there is an organic relationship among the chemical compositions. The coefficients of proportionality between compositions are often used to study some chemical problems in hydrological earth (Anita and Gita, 2011). The MEq concentration ratio (γ_{Na}/γ_{Cl}) is called the genetic factor of underground water. It is a hydrogeochemical parameter to characterize the enriching of Na^+ (Chen et al., 2012). The average value of γ_{Na}/γ_{Cl} for seawater is 0.85. There is a higher value for low salinity water ($\gamma_{Na}/\gamma_{Cl} > 0.85$) and a lower value for concentrated water ($\gamma_{Na}/\gamma_{Cl} < 0.85$) (Aghazadeh and Mogaddam, 2011). In the shallow water of Tongchuan City, the γ_{Na}/γ_{Cl} value of γ_{Na}/γ_{Cl} is in the range from 0.75 to 15.41, with an average value of 2.90. Among them, most of the samples have a γ_{Na}/γ_{Cl} value of less than 1 (as shown in Figure 2) and only two samples are larger than 1. In deep water, the value of γ_{Na}/γ_{Cl} is in

the range from 2.3 to 36.25, with an average value of 13.01. The values of all samples are larger than 1. Above results demonstrate that in the runoff process, the water is hydrolyzed and acidized, which releases Na^+ from soil and aquifers (Ahmad Dar et al., 2011). There is also ion exchange between Ca^{2+} from water and Na^+ from the soil, which results in $\gamma_{Na} > \gamma_{Cl}$. The value of γ_{Na}/γ_{Cl} is higher in deep water than that of shallow water, which may be caused by the long time lixiviation and replacing (Figure 3).

Research has demonstrated that the value of $\gamma_{Na}/(\gamma_{Na} + \gamma_{Cl})$ could reflect the exchange of positive ions. When the value is larger than 0.5, it means the exchange of positive ions happens. After the Na of soil and aquifers are replaced by Ca and Mg in water, it flows into underground water. The value of $\gamma_{Na}/(\gamma_{Na} + \gamma_{Cl})$ is in the range from 0.429 to 0.939, with an average value of 0.665. Among them, there are only two samples, whose value of $\gamma_{Na}/(\gamma_{Na} + \gamma_{Cl})$ is less than 0.5. In the deep water, the value of $\gamma_{Na}/(\gamma_{Na} + \gamma_{Cl})$ is in the range from 0.697 to 0.973, with an average value of 0.848. The values of all samples are larger than 0.5 and higher than that in shallow water. Above results demonstrate that there is different degree of cations exchange adsorption and the deep water has a relatively strong adsorption. This leads to the fact that with the increasing of depth the advantage ion turns to be Na^+ from Ca^{2+} .

As seen in Figure 4, the ratio of $\gamma_{HCO_3^-} + \gamma_{SO_4^{2-}}$ and $\gamma_{Ca^{2+}} + \gamma_{Mg^{2+}}$ is close to 1. Above results demonstrate that the underground water is mainly from rainfall and the ions of Ca^{2+} , Mg^{2+} and HCO_3^- are mainly from the weathering dissolution of carbonate rock. The ratio of $\gamma_{HCO_3^-} + \gamma_{SO_4^{2-}}$ and $\gamma_{Ca^{2+}} + \gamma_{Mg^{2+}}$ is larger than 1:1, which demonstrates that the contents of Ca^{2+} and Mg^{2+} have dramatically decreased.

Classification of underground water

According to the classification method of Shug Kalev, the

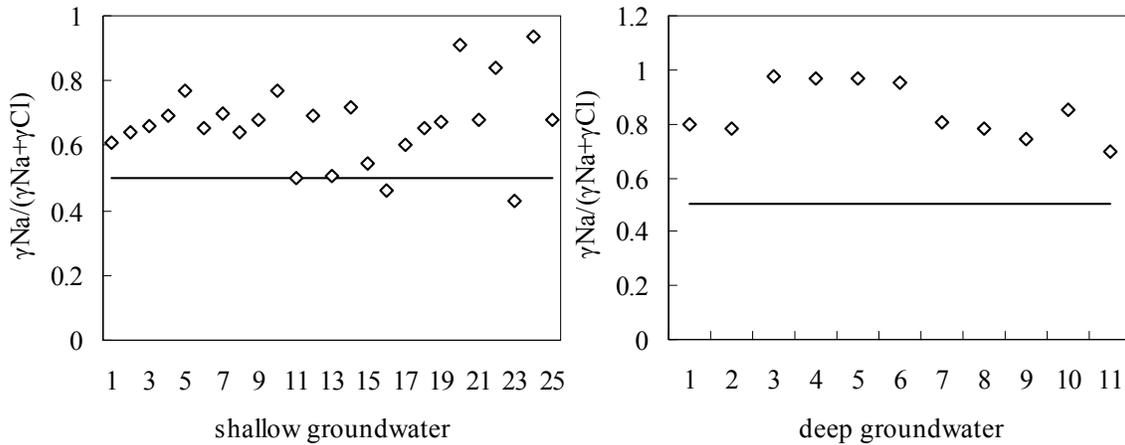


Figure 3. Scattergram of $\gamma\text{Na}/(\gamma\text{Na}+\gamma\text{Cl})$ values of groundwater.

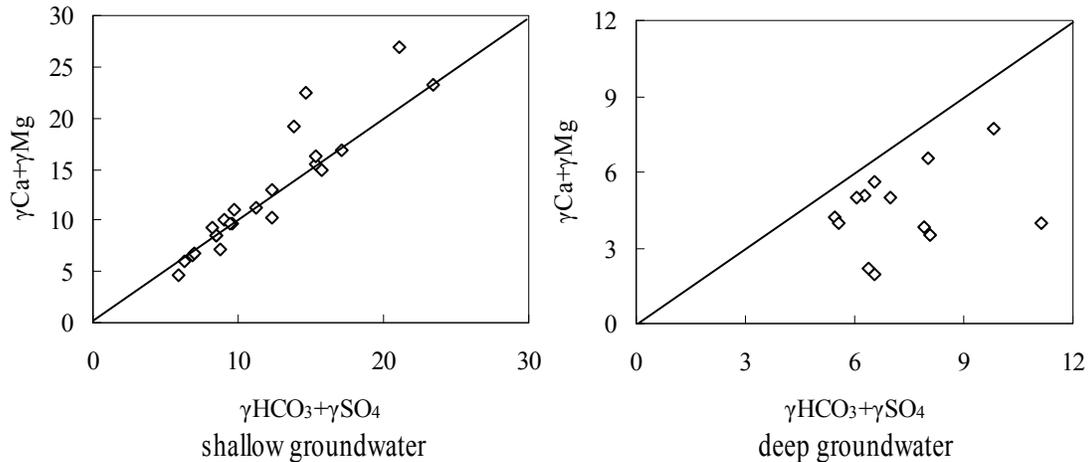


Figure 4. Scattergram of $(\gamma\text{HCO}_3+\gamma\text{SO}_4)/\gamma\text{Ca}+\gamma\text{Mg}$ values of groundwater.

samples of underground water in Tongchuan City can be divided into 22 types as shown in Table 3. There are various categories of hydrochemical types. Among them, the type $\text{HCO}_3\text{-SO}_4\text{-Ca}$ accounts for the largest proportion, which is 10.26% of the samples (4 samples). For other samples, $\text{HCO}_3\text{-Ca}\cdot\text{Na}\cdot\text{Mg}$, $\text{HCO}_3\text{-N}$ and $\text{HCO}_3\text{-SO}_4\text{-Ca}\cdot\text{Na}\cdot\text{Mg}$ accounts for 7.69% proportion (3 samples). There are 15 kinds of water samples in shallow water. The type of $\text{HCO}_3\text{-SO}_4\text{-Ca}$ accounts for the largest proportion, followed by $\text{HCO}_3\text{-Ca}$, $\text{HCO}_3\text{-Ca}\cdot\text{Mg}$, $\text{HCO}_3\text{-SO}_4\text{-Ca}\cdot\text{Na}$, $\text{HCO}_3\text{-SO}_4\text{-Ca}\cdot\text{Na}\cdot\text{Mg}$, $\text{SO}_4\text{-Ca}$, $\text{SO}_4\text{-Ca}\cdot\text{Mg}$ and $\text{SO}_4\text{-HCO}_3\text{-Ca}$ water types. There are 10 kinds of water types in deep water, with type $\text{HCO}_3\text{-Na}$ as the largest. Then, they are $\text{HCO}_3\text{-Ca}\cdot\text{Na}\cdot\text{Mg}$ and $\text{HCO}_3\text{-Ca}\cdot\text{Na}$ type water as shown in Table 3. We can conclude that the types of water chemistry of shallow groundwater are complex and the deep water is relatively simple. Generally, the hydrochemical types of shallow water are

simpler than that of deep water. This is caused by the longer time of leaching and replacing, which makes the composition of water more complex. The adverse consequences are caused by the contamination of shallow water.

Features of the hydrochemical evolution

We obtained the Piper trilinear chart using software of ‘information system of groundwater pollution investigation’ as seen in Figure 5. It can be concluded that there are obvious differences in the chart of shallow and deep waters. In the shallow water, the positive ions mainly consist of Ca^{2+} and the concentration of Na^+ and K^+ are relative low. In deep water, the positive ions mainly consist of Na^+ and K^+ . The concentration of Mg^{2+} and Ca^{2+} are relative low. The negative ions of shallow water

Table 3. Hydrochemical type of groundwater.

	Hydrochemical type	Sample number	Ratio (%)
Shallow groundwater	HCO ₃ ·SO ₄ -Ca	4	16
	HCO ₃ -Ca	2	8
	HCO ₃ -Ca·Mg	2	8
	HCO ₃ ·SO ₄ -Ca·Na	2	8
	HCO ₃ ·SO ₄ -Ca·Na·Mg	2	8
	SO ₄ -Ca	2	8
	SO ₄ -Ca·Mg	2	8
	SO ₄ ·HCO ₃ -Ca	2	8
	HCO ₃ -Ca·Na·Mg	1	4
	HCO ₃ ·SO ₄ -Ca·Mg	1	4
	HCO ₃ ·SO ₄ -Na·Mg	1	4
	SO ₄ ·Cl-Ca	1	4
	SO ₄ ·Cl·HCO ₃ -Mg·Ca	1	4
	SO ₄ ·HCO ₃ -Ca·Mg	1	4
	SO ₄ ·HCO ₃ -Ca·Na	1	4
	Deep groundwater	HCO ₃ -Na	3
HCO ₃ -Ca·Na·Mg		2	14.29
HCO ₃ -Ca·Na		2	14.29
HCO ₃ -Mg·Na·Ca		1	7.14
HCO ₃ -Mg·Ca·Na		1	7.14
HCO ₃ -Na·Mg		1	7.14
HCO ₃ -Na·Ca		1	7.14
HCO ₃ ·SO ₄ -Na·Ca·Mg		1	7.14
HCO ₃ ·SO ₄ -Na·Mg		1	7.14
HCO ₃ ·SO ₄ -Ca·Na·Mg		1	7.14

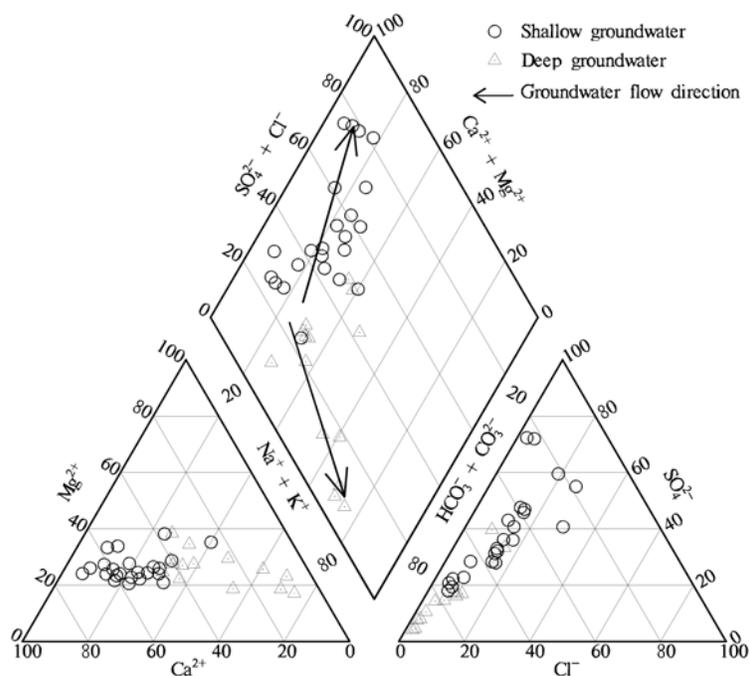


Figure 5. The piper diagram for the groundwater samples.

mainly consist of HCO_3^- and SO_4^{2-} . The concentration of Cl^- is relatively low. In deep water, the negative ions mainly consist of HCO_3^- and the concentration of Cl^- and SO_4^{2-} are relatively low. Along the direction of flow, the change of negative ions in deep water is not obvious. The ratio of positive ions increases and the concentration of Ca^{2+} and Mg^{2+} decrease. With the increase of runoff channels, the Na^+ in water-bearing media has exchanged with Ca^{2+} and Mg^{2+} in water. The type of underground water turns to be $\text{HCO}_3\text{-Na}$ from $\text{HCO}_3\text{-Mg}\cdot\text{Ca}\cdot\text{Na}$ and $\text{HCO}_3\text{-Ca}\cdot\text{Na}$. Along the direction of flow, there is no obvious exchange in the positive ions of shallow water and the change of negative ions are obvious. With the increasing of SO_4^{2-} , the concentration of HCO_3^- decreases and the concentration of Cl^- is almost the same. The increasing of SO_4^{2-} means the contamination is more serious along the flow, which has a relationship with the city and industrial zone in the downstream region. The types of water turn to $\text{SO}_4\text{-Ca}\cdot\text{Mg}$, $\text{SO}_4\cdot\text{HCO}_3\text{-Ca}\cdot\text{Na}$ from $\text{HCO}_3\text{-Ca}$, $\text{HCO}_3\text{-Ca}\cdot\text{Mg}$.

Generally, as for underground water, the containment of alkaline earth metal is larger than that of alkali metal. For the deep water, the containment of weak acid is larger than that of strong acid. In the upstream area, both the carbonate hardness of shallow and deep waters are higher than 50%. The feature of water is mainly weak acid and alkaline earth metal, which suggests that the formation of water is mainly from carbonate leaching. With the flowing of water, carbonate hardness of deep water becomes higher than 50% and the content of alkali metal is larger than alkaline earth metal. The underground water changes into weak acid and alkali metal.

Distribution characteristics of hydrochemical type

The underground water of North Ziwuling mountain area is mainly bedrock fissure water. The most common type of water is $\text{HCO}_3\text{-SO}_4\text{-Ca}$. In this area, the water is mainly provided by atmospheric precipitation. The runoff is beyond compare and the stay time is relatively short in aquifer. The water is easy to exchange with the environment and the soluble components, such as Cl^- , Na^+ and K^+ . Most of the ions are Ca^{2+} , HCO_3^- and SO_4^{2-} , which can form the water type of $\text{HCO}_3\text{-SO}_4\text{-Ca}$. The underground water of Qishui River Valley Area, from south Zhifang to stream outlet, is alluvium pore water. From upstream to downstream, the water type changes into $\text{HCO}_3\text{-SO}_4\text{-Ca}\cdot\text{Na}$ from $\text{HCO}_3\text{-SO}_4\text{-Ca}$. Especially, the composition of some areas are complex and the water type is $\text{HCO}_3\text{-SO}_4\text{-Ca}\cdot\text{Na}\cdot\text{Mg}$. The contents of negative ions are relatively stable and the concentration of Na^+ gradually increases. The value of TDS is also increased. The underground water of Wang River Valley, from south Aipu village to stream outlet, is shallow fissure water. From upstream to downstream, the water type

changes into $\text{SO}_4\cdot\text{HCO}_3\text{-Ca}\cdot\text{Mg}$ from $\text{HCO}_3\text{-SO}_4\text{-Ca}$. There is an increase in the concentration of SO_4^{2-} and Mg^{2+} . The TDS rises from 621.1 to 1318 mg/L. The underground water of Guangyang River Valley, west of Guangyang town, is alluvium pore water. From upstream to downstream, the water type changes into $\text{SO}_4\cdot\text{HCO}_3\text{-Ca}\cdot\text{Mg}$ from $\text{HCO}_3\text{-Ca}$. There is a gradual increase in the concentration of SO_4^{2-} and Mg^{2+} . The TDS rises from 458.4 to 1586 mg/L. The underground water of southern Sichuan area is mainly alluvial pore water. Most of the water is deeply confined water and the water type is mainly $\text{HCO}_3\text{-Na}$. The underground water of valley area is mainly $\text{HCO}_3\text{-Ca}\cdot\text{Na}\cdot\text{Mg}$. The type of underground water is simplex. The TDS is in the range from 400 to 600 mg/L. The concentration of Na^+ is high, which is mainly affected by loess components. The water yield for gully region of Loess Plateau is small. The sample is relatively shortage. After reading papers, we know that the water type is mainly $\text{HCO}_3\text{-Ca}\cdot\text{Mg}$. There are other types, such as $\text{HCO}_3\text{-SO}_4\text{-Na}\cdot\text{Mg}$, $\text{HCO}_3\text{-Mg}\cdot\text{Ca}\cdot\text{Na}$, $\text{HCO}_3\text{-Mg}\cdot\text{Na}\cdot\text{Ca}$ and $\text{SO}_4\cdot\text{HCO}_3\text{-Ca}$. The negative ions are mainly HCO_3^- . The sample of karst water is in relative shortage. After reading papers, we conclude that the water types are mainly $\text{HCO}_3\text{-SO}_4\text{-Na}\cdot\text{Ca}\cdot\text{Mg}$ and $\text{HCO}_3\text{-SO}_4\text{-Ca}\cdot\text{Na}\cdot\text{Mg}$. The water type of Ju and Qishui Rivers are both $\text{HCO}_3\text{-SO}_4\text{-Ca}$. There are close connections between the water and shallow water, which is an important reason for the high concentration of SO_4^{2-} . It is also the source of SO_4^{2-} in karst water. Recently, with the exacerbating of contamination, the name of some area stems from its region. When considering hydrogen nitrate using the method of Shug Kalev, there are six groups of samples that belongs to hydrogen nitrate types. Telling from the distribution, it is mainly focused on the area of southern Chuanyuan and the area along the QI River. The area of southern Chuanyuan is the main farmland area. Compared with loess tableland, it has more water and the land has more fertilizer. The pollution is more serious than that of loess tableland. Above factors may act as the reasons for the forming of hydrogen nitrate type.

Conclusion

The salinization of shallow underground water in Tongchuan City is determined by the SO_4^{2-} , NO_3^- , Cl^- and K^+ . In deep water, the contents of SO_4^{2-} , NO_3^- , Cl^- are largely different and other indexes are relatively stable. The values of $\gamma_{\text{Na}}/\gamma_{\text{Cl}}$ demonstrate that the process of runoff makes the Na^+ release from soil and aquifer and there is exchange between the Ca^{2+} in water and Na^+ in soil, which leads to $\gamma_{\text{Na}} > \gamma_{\text{Cl}}$. Due to long time leaching and replacing, the cation exchange adsorption is very sufficient in deep water. This leads to a higher $\gamma_{\text{Na}}/\gamma_{\text{Cl}}$ value than that of shallow water. The value of $\gamma_{\text{Na}}/(\gamma_{\text{Na}} + \gamma_{\text{Cl}})$ demonstrates that with the increasing of underwater depth, the cation exchange adsorption increases, which

leads to the advantage ion change into Na^+ from Ca^{2+} . The ratio of $\gamma_{\text{HCO}_3} + \gamma_{\text{SO}_4}$ and $\gamma_{\text{Ca}} + \gamma_{\text{Mg}}$ demonstrates that the shallow water mainly stems from rainfall and the effects of cation exchange are more obvious in deep water.

The type of underground water in Tongchuan City is mainly $\text{HCO}_3 \cdot \text{SO}_4 \cdot \text{Ca}$. Its hydrochemical types are relatively complex. It is mainly $\text{HCO}_3 \cdot \text{Na}$ in deep water. As for the shallow water, the content of weak acid is larger than that of strong acid. In the upstream area, the shallow water mainly consists of weak acid and alkaline earth metal. Its components are mainly carbonated leaching. With the flowing of water, the shallow water changes into strong acid and alkaline earth metal and the deep water change into weak acid and alkali metal.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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