Identification of the hydrogeochemical processes and assessment of groundwater quality using classic integrated geochemical methods in the Southeastern part of Ordos basin, China

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ABSTRACT

Insufficient understanding of the hydrogeochemistry of aquifers makes it necessary to conduct a preliminary water quality assessment in the southern region of Ordos Basin, an arid area in the world. In this paper, the major ions of groundwater have been studied aiming at evaluating the hydrogeochemical processes that probably affect the groundwater quality using 150 samples collected in 2015. The two prevalent hydrochemical facies, $HCO_3-Mg\cdot Na\cdot Ca$ and $HCO_3-Mg\cdot Ca\cdot Na$ type water, have been identified based on the hydrochemical analysis from Piper trilinear diagram. Compositional relations have been used to assess the origin of solutes and confirm the predominant hydrogeochemical processes responsible for the various ions in the groundwater. The results show that the ions are derived from leaching effect, evaporation and condensation, cation exchange, mixing effect and human activities. Finally groundwater quality was assessed with single factor and set pair methods, the results indicate that groundwater quality in the study region is generally poor in terms of standard of national groundwater quality. The results obtained in this study will be useful to understand the groundwater quality status for effective management and utilization of the groundwater resource.

1. Introduction

Water shortage has become an increasingly serious problem in China, especially in arid and semi-arid zones, groundwater plays a major role in the water supply of arid and semiarid regions, and is gaining increasing importance in the supply of water to rural communities. It is estimated that approximately one-third of the world's population use groundwater for drinking (Nickson et al., 2005). Knowledge on hydrogeochemical characteristics plays an important role in assessing the groundwater quality to understand its suitability for various purposes. Therefore, it is necessary to understand the hydrochemical characteristics of the groundwater and its evolution under natural water cycle processes for sustainable development and effective groundwater management (Wen et al., 2005; Tizro and Voudouris, 2008; Chang and Wang, 2010). The groundwater chemistry depends on different

hydrogeochemical processes that the groundwater undergoes over space and time. The variation of groundwater quality is the combined effects of natural and anthropogenic factors, such as geological structure where groundwater is stored, composition of precipitation, the interaction between the groundwater and aquifer minerals like oxidation/reduction, cation exchange, precipitation/dissolution of minerals, mixing of waters, leaching of fertilizers, manure, biological and micro-biological process, and human activities. The interaction of these factors result in various groundwater types. Hydrogeochemical study is usually considered to be useful in identifying these processes that control groundwater hydrochemistry (Jeevanandam et al., 2007). Generally, the ions of groundwater is controlled by many factors that include recharged water, atmospheric precipitation, and inland surface water and on subsurface geochemical processes. The interaction of all factors leads to various water types. The increased knowledge of geochemical processes can help to understand the groundwater hydrogeochemical systems.

Research on water quality and hydrochemistry has been widely conducted over the world due to the increasing awareness of water

quality protection. In recent years, many works are focused on the study of natural water and environment of the northern part of Ordos Basin, understanding the relationships between water and environment, water and development, and recognizing how to practice sound water management (Dong et al., 2008; Su et al., 2009; Hou et al., 2006). And the groundwater quality in the southeastern part of Ordos Basin has received little attention for decades, and no international literature can be viewed up to date. The southern part of Ordos Basin is predominantly covered by loess with broken terrains and strong cuttings. The scarce precipitation and strong evaporation result in the sparse vegetation in most part of the area, subsequently desertification and soil erosion gives rise to the fragile eco-environment. At present, water shortage has become a hinder of local economic development. Therefore, the investigation of hydrochemistry of this area has become a high-priority concern to the whole community. Therefore, a comprehensive hydrogeochemical study is necessary to identify the chemical processes that affect the groundwater quality of this area. Under these circumstances, a national research project named "Investigation on Groundwater Pollution in Ordos Basin" was carried out in 2015 at the southeastern part of Ordos Basin to interpret the chemistry of groundwater and assess the groundwater quality.

This paper is constructed with an effort to interpret the main hydrogeochemical processes controlling groundwater compositions in the southeastern Ordos Basin using Piper trilinear diagram, ionic ratio coefficient, principal component analysis, and further to assess groundwater quality with single factor analysis and set pair evaluation methods.

2. Study area

The Ordos Basin is located in the middle reaches of the Yellow River in the northwest of China. It is surrounded by mountains all sides, Qinling, Yinshan, Lv Liangshan, Helan - six panshan mountains in north, south, east and west, respectively. The region of this study is the southeastern part of Ordos Basin, which lies between 108°12′-111°17′ E and 34°26′-37°29′ N, covering a total area of 67781 km^2. The area is mainly covered by loess and Pliocene mudstone with broken terrain and typical cutting, which is not favorable to recharge. Due to the asymmetry of the total basin, the carboniferous - Jurassic clastic rock underlying (the top of Paleozoic carbonatite) outcropped at the southeast of the basin as an unconformable denudation, the aquifer is usually cut through by surface water and can get recharged from surface water and precipitation. The main water system from west to East followed by Cambrian - Ordovician karst water system, Cretaceous groundwater system, Carboniferous and Jurassic fissure water and overlying loose pore water system with poor hydraulic connection. The area is characterized with continentally arid and semi-arid climate.

3. Sampling and analytical procedure

3.1. Sample collection and measurement

150 water samples were collected from 150 wells during June to July 2015 in the Southeastern part of the Ordos Basin. Fig. 1 shows the locations of the selected wells. These wells are numbered from 1 to 150. All these samples were analyzed in the laboratory for major ions. During sample collection, handling, and preservation, standard procedures recommended by the Standard Examination Methods for Drinking Water were followed to ensure data quality and consistency (Ministry of Health of the People's Republic of China (2006)). Charge balanced-alkalinity (alkalinity hereafter) was calculated by $[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] - [Cl^-] - [NO_3^-] - [SO_4^{2-}]$ in mmol/l (Reuss and Johnson, 1986). The analytical

precision for the measurements of ions was determined by the ionic balances, calculated as 100 × (cations − anions)/ (cations + anions), which is generally within ±5%.

3.2. Analytical methods

Piper diagram is one of the most effective graphic representation in the study of the groundwater quality, which helps to understand the groundwater geochemical characteristics. In this paper, the water chemical analysis software AquaChem V4.0 was used to draw the piper diagram of the selected samples, which can directly reflect the general chemical characteristics of water samples and the relative content of various ions (Purushotham et al., 2011; Hong, 2012). Ionic ratio coefficient method and principal component analysis method were applied to chemical data for analyzing the main characteristics of ion composition and ion proportion in groundwater, so as to determine the geochemical process of groundwater.

In order to determine the suitability in terms of domestic and agricultural purposes, Single factor analysis and set pair evaluation method are two commonly used methods in groundwater quality assessment. In order to improve the accuracy of assessment results of groundwater quality, single factor analysis method was performed first. That is, the analysis and evaluation of each index in all samples were carried out in accordance with the "groundwater quality standards" DZ/T 0209-2015 (Ministry of Land and Resources of P. R. China, 2015) and the final evaluation class is determined using the highest level of groundwater samples. The second step is performing set pair method by selecting the components which have an important effect on water quality as evaluation factors. Finally, GIS was used to show visually the evaluation results.

4. Results and discussion

4.1. Groundwater chemistry

4.1.1. Hydrochemical facies
Hydrochemical facies is a term used to describe the quantities of water differing in their chemical compositions, which is a combined effects of solution kinetics, rock-water interactions, hydrogeological settings and contamination sources. A convenient method to determine groundwater types based on ionic composition, Piper trilinear diagram, was proposed by Piper (1944), which consists of a diamond and a pair of equilateral triangles, two triangles are respectively represent the anion and cation and the two triangles are connected by a diamond shaped diagram. The Piper diagram was constructed using AquaChem V4.0, which can visually show the relative concentrations of the different ions of each water sample. The chemical groundwater types of the study area were distinguished and grouped by their position on a Piper diagram (Fig. 2). Based on the major cation and anion, 5 major hydrochemical facies were identified, they are: $HCO_3-Mg\cdot Na\cdot Ca$, $HCO_3-Mg\cdot Ca\cdot Na$, $HCO_3-Ca\cdot Mg$, $HCO_3-Na\cdot Mg\cdot Ca$, and $HCO_3-\oplus$ $Na\cdot Mg$ types.

4.1.2. Descriptive statistics
Cv (Coefficient of variation) is usually used to characterize the stability of variable. When the 0 < Cv < 10 percent for weak mutation; 10% < Cv < 100% for moderate variability; Cv>100% strong variation. In this paper, the statistical analysis results of 150 groundwater samples in 2015 for each water quality parameter from study area are presented in Table 1.

The pH value in the study area ranges from 7.17 to 8.32 with a mean value of 7.74 and standard deviation of 3.4%, indicating a weakly alkaline environment. These values were found to be in the
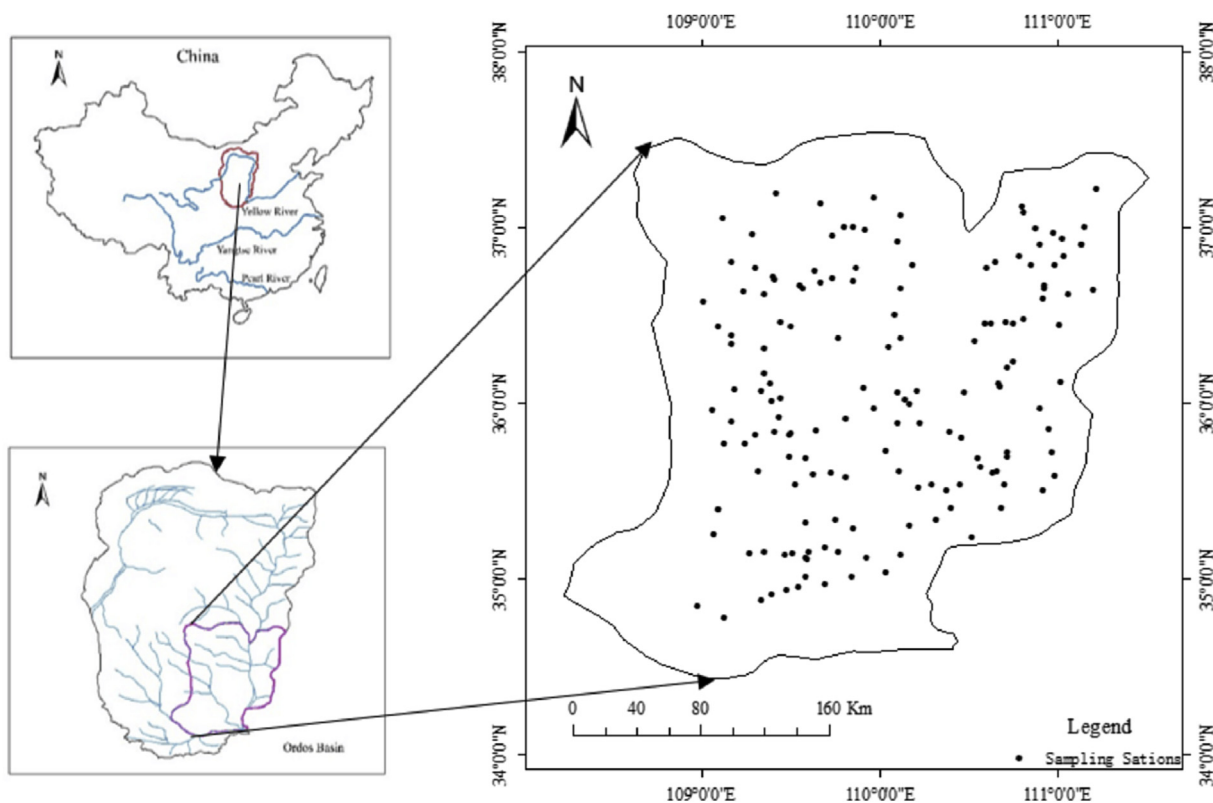
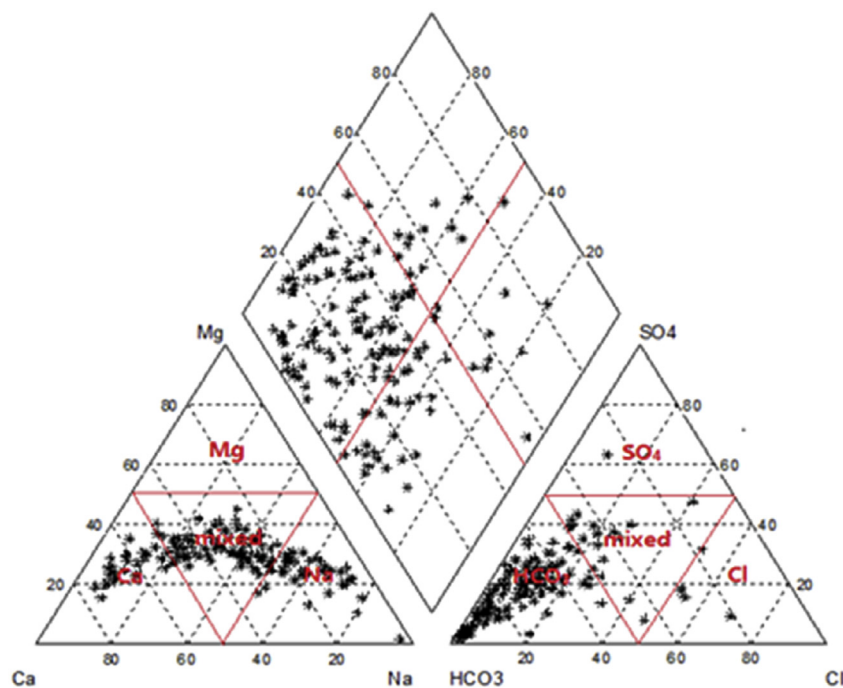**Fig. 1.** Location and sampling points of the research area.

Fig. 2. Piper trilinear diagram of groundwater.

permissible range of 6.5—8.5. Fig. 3 shows that the order of relative abundance of major cations in the groundwater of the study area is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$, accounting for 48.203%, 32.528%, 18.087% and 1.183% of all the cations, respectively. The order of relative abundance of major anions is $HCO_3^- > SO_4^{2-} > Cl^-$, contributing 70.523%, 18.530% and 10.948% of the total anions, respectively. The concentrations variation coefficient of K^+, Cl^-, SO_4^2 and NO_3^- in study area is relatively large, indicating that these ions are more sensitive and unstable to external inputs, such as the hydrological conditions, topography, and anthropogenic activities.

Table 1
Statistical summary of parameters in groundwater samples.

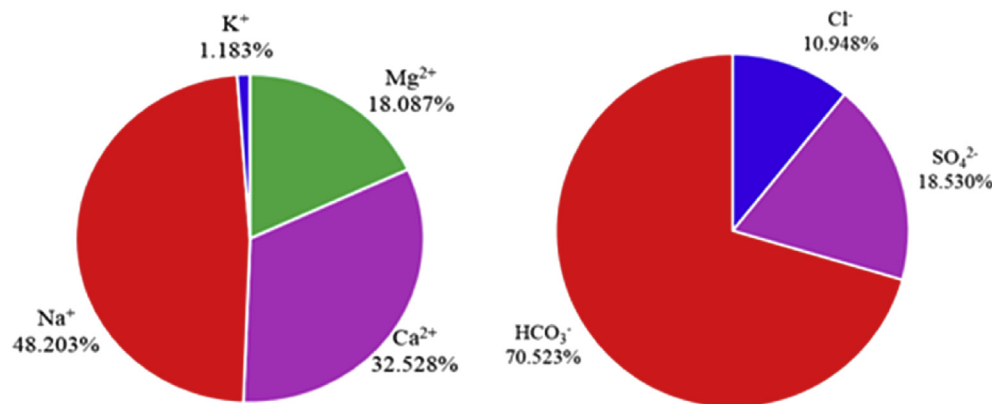| Parameters	Max	Min	Mean	Cv (%)
K^+(mg/L)	19.10	0.42	2.47	126.88
Ca^{2+}(mg/L)	234.00	6.72	67.84	59.03
Mg^{2+}(mg/L)	163.00	1.99	37.72	65.35
Na^+(mg/L)	558.00	5.24	100.54	93.56
Cl^-(mg/L)	656.51	2.41	61.94	166.15
HCO_3^-(mg/L)	805.00	172.00	399.03	29.32
SO_4^{2-}(mg/L)	765.81	2.23	104.84	106.54
NO_3^-(mg/L)	460.93	0.29	42.29	153.75
NH_4^+(mg/L)	0.18	0.00	0.03	85.49
pH	8.32	7.17	7.74	3.40
COD	3.25	0.66	0.30	45.45
TDS(mg/L)	2579.00	219.00	653.77	68.30

Niranjan, 2010) and ion exchange reaction.

Trends of K^+/Cl^- versus Cl^- shown in Fig. 4b reveals K^+/Cl^- ratio (>0.2) is most likely associated with the dissolution and weathering of K-feldspar (Chang and Wang, 2010) with the following reaction:

$$K_2Al_2Si_6O_{16} + 2H_2O + CO_2 \rightarrow K_2CO_3 + H_2Al_2Si_2O_8 + H_2O + 4SiO_2$$

The dissolutions of calcite, dolomite and gypsum are the prevalent reactions in a system if the ratio of $(Ca^{2+} + Mg^{2+})$ versus $(HCO_3^- + SO_4^{2+})$ is close to the 1:1 line. The plot of $(Ca^{2+} + Mg^{2+})$ versus $(HCO_3^- + SO_4^{2+})$ fall above the 1:1 line, and indicate mainly the dissolution of silicate and sulfate minerals (Su et al., 2009). Fig. 4c shows that the plot of $(Ca^{2+} + Mg^{2+})$ versus $(HCO_3^- + SO_4^{2+})$

Fig. 3. Pie diagram of median values of major ions.

4.1.3. Identification of hydrogeochemical processes

Water-rock interactions play a significant role on the variations of groundwater quality, which are also useful to determine the genesis of groundwater. Ratio of the various components of groundwater is often used to analyze the concentration of different major elements and their interrelationship, and to understand and illustrate hydrogeochemical processes and also the origin of the chemical compositions (Kumar et al., 2014; Yang et al., 2016). Various conventional graphical plots are often employed to identify the hydrogeochemical processes occurred in the aquifer. Several possible processes are explained below.
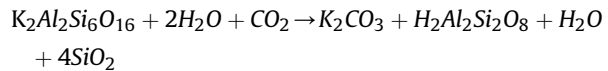
4.1.4. Leaching effect

Leaching effect means the transfer of rock materials into groundwater during the interaction process between water and rock, resulting partial loss of the soluble substance and a new supplement component to groundwater.

The Na^+–Cl^- relationship has often been used to identify the mechanisms for acquiring salinity and saline intrusions in semi-arid regions. If sodium comes from only halite dissolution, the Na^+/Cl^- ratio is approximately 1 (Meybeck, 1987). Fig. 4a shows the value of Cl^- as a function of Na^+ in groundwater samples. However, the analytical data in Fig. 4a deviate from the expected 1:1 relation line (96% of samples fall above 1:1 line), indicating that Na^+ has other sources. The low concentration of Na^+ and Cl^- in groundwater indicates that the dissolution of halite is not the dominant source of Na^+ in groundwater, the excess of Na^+ and Cl^- in the groundwater may come from wastewater. Usually wastewater is enriched in Na^+ relative to Cl^- (Vengosh and Keren, 1996), or probably is released from silicate weathering reaction (Kumar et al., 2009; Joseph Richmond Fianko et al., 2010; Reddy and Kumar

fall near and below the 1:1 line except for several samples, indicating that the dissolution of carbonate and silicate minerals or sulfate minerals contributes most to groundwater chemical components. The points above the 1:1 line are assumed to the result of cation exchange (Cerling et al., 1989; Fisher and Mulican, 1997).

The ratio Ca^{2+}/Mg^{2+} is an indicator for studying the dissolution of the major minerals. Fig. 4d shows that the samples distribute uniformly beside $Ca^{2+}/Mg^{2+} = 1$ line. $Ca^{2+}/Mg^{2+}<1$ (44% of the total samples) suggests that the water rock reaction in the study area is mainly dominated by the dissolution of dolomite, this process takes place most in the northern and southern part of the study area. $Ca^{2+}/Mg^{2+} > 1$ (56% of the total groundwater samples) is caused probably by dissolution of calcite and gypsum minerals (Maya and Loucks, 1995), which primarily lies in the central and the southwestern regions of the study area. Because of the relatively low content of gypsum in the study area, a bulk of the Ca^{2+} content in the groundwater is most likely attributed to the dissolution of carbonate minerals.

The ratio of Ca^{2+}/SO_4^{2+} and Mg^{2+}/SO_4^{2+} is illustrated in Fig. 4e and f. A very slight correlation between Ca^{2+} and SO_4^{2+} was found, with a value of correlation coefficient 0.121, and that of Mg^{2+} and SO_4^{2+} is 0.399. Deviation from the 1:1 line indicates another source of SO_4^{2+}. It also indicates that the solubility of gypsum and anhydrite were weak in the study area, other processes such as mineral weathering, gain or loss of less soluble salts (gypsum) ion exchange reactions and long-term solute transport. The industrial and agricultural activities also can result in the increase of Mg^{2+} and SO_4^{2+} ions in groundwater except for mineral weathering and water-rock interactions. On the other hand, the high sulfate concentration in groundwater possibly was derived from the fertilizer and the leaching of coal mine.
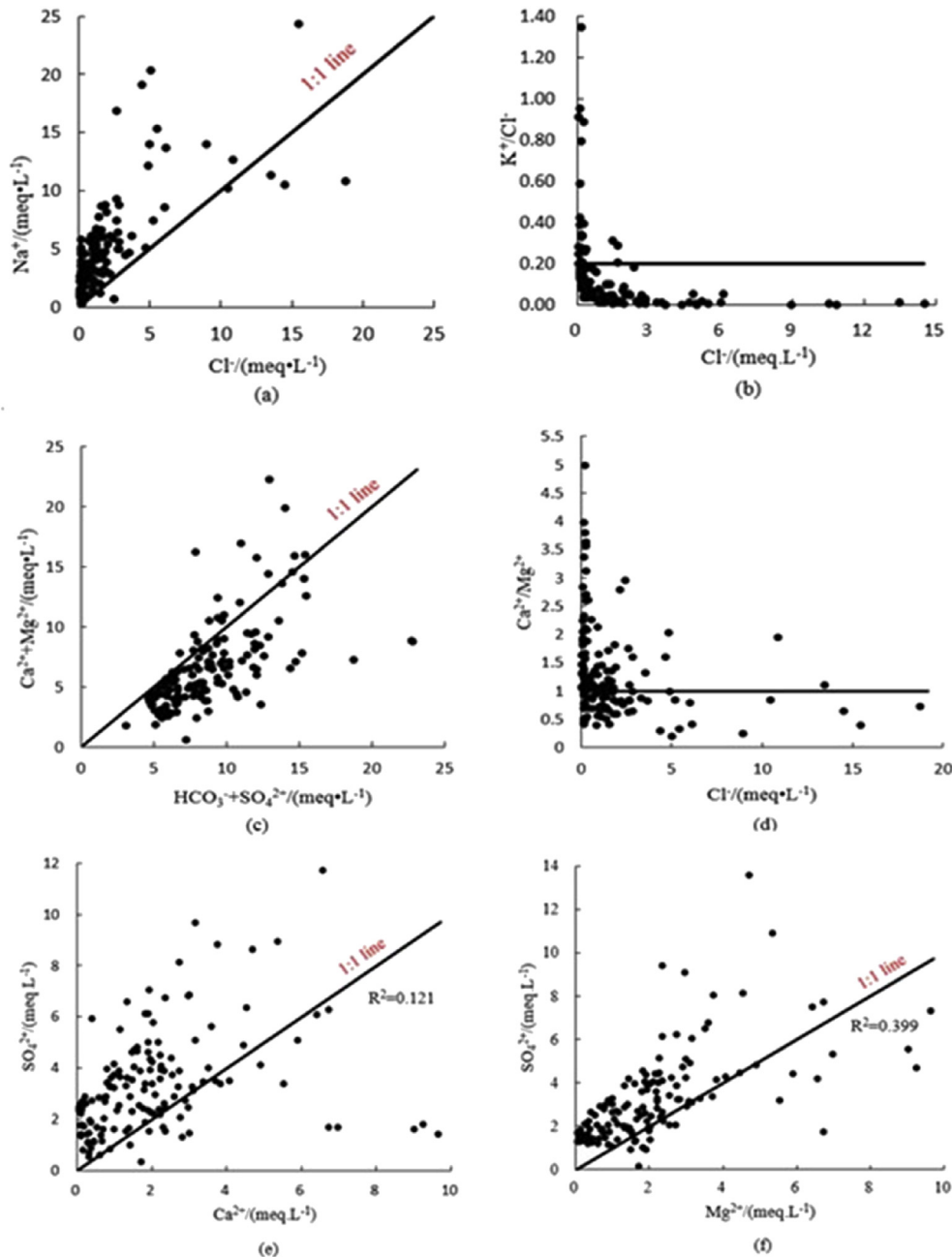
Fig. 4. Relationships between ion concentrations.

The chemical data of the groundwater samples are plotted on the Mg^{2+} versus alkalinity diagram (Fig. 5g). It can be seen that there is a slight correlation between Mg^{2+} and alkalinity with a correlation coefficient of 0.33. Majority of the data fall below the equiline (1:1), which suggests that an excess of alkalinity in the water has been balanced by alkalies (Rao, 2008; Ganyaglo, 2012). A 1:1 relationship between alkalinity and (Ca^{2+} + Mg^{2+}) would be expected from the dissolution of dolomite. There exists a poor relationship between alkalinity and (Ca^{2+} + Mg^{2+}) (R^2 = 0.22) (Fig. 5h), indicating that dolomite dissolution in the basin is not the unique source of Ca^{2+} and Mg^{2+} in the groundwater. There is a very poor relationship between alkalinity and Ca^{2+} (Fig. 5i) with a value of correlation coefficient 0.07, which demonstrates also the decrease of Ca^{2+} was caused by cation exchange. The poor

correlation (R^2 = 0.19) between alkalinity and Na^+ also indicates the dissolution of sodium carbonate is not significant in the study area. In summary, the hydrochemical facies are interpreted as the dissolution of carbonates, silicates and halite.

4.1.4.1. Evaporation and condensation. As the research area is located in the arid and semi-arid Loess Plateau and the sub area of the intermountain basin, the precipitation is scarce and the underground runoff is weak, which provides a favorable condition for the evaporation and condensation. Due to the solubility of halite, Cl^- content increases with the increase of the salinity, and is not absorbed by plants, bacteria and soil particle surface (Shen, 1993). As a result of evaporation, Cl^- content in the groundwater in arid area is relatively higher, so it can reflect the mineralization degree
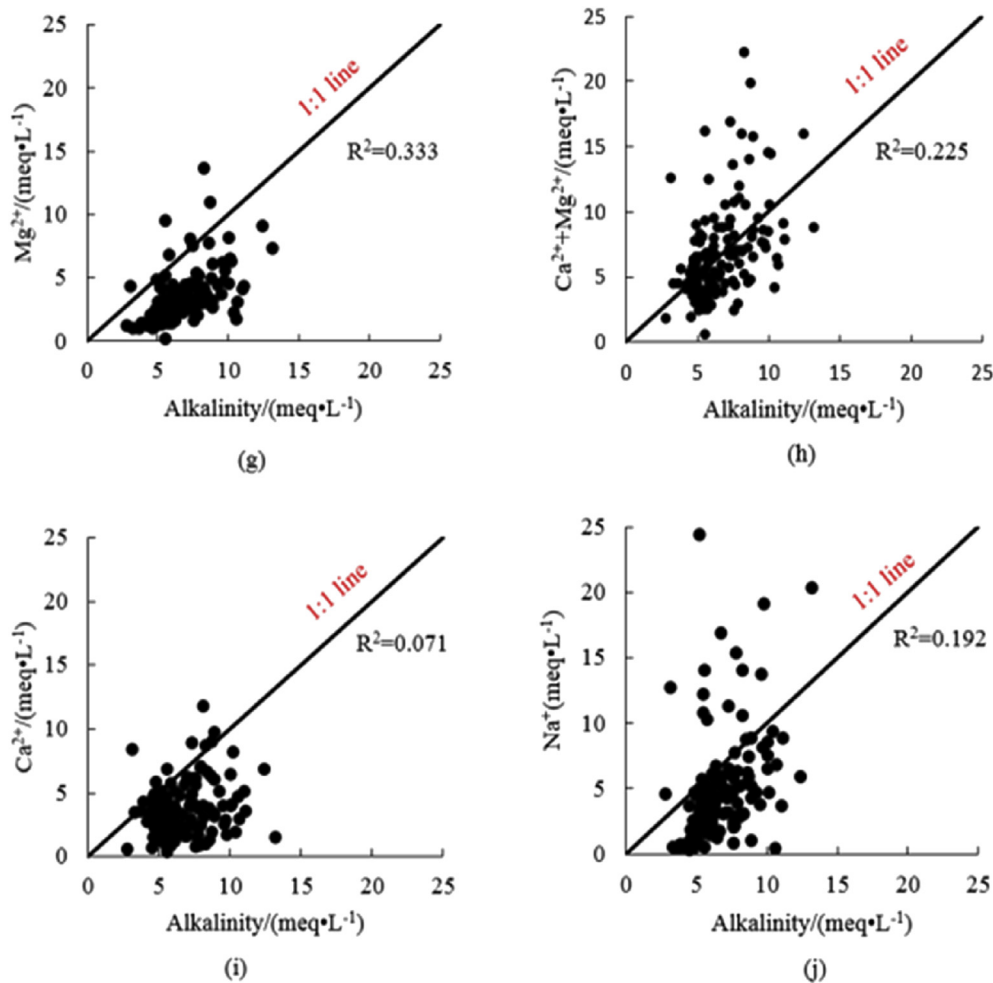
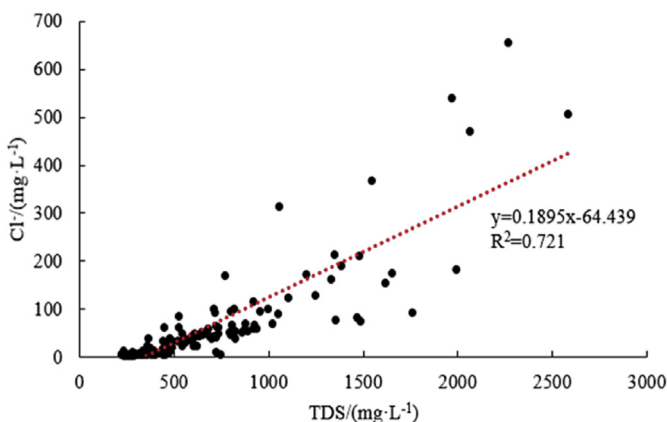Fig. 5. Relationship between Ca^{2+}, Mg^{2+}, Na^+ and alkalinity.

Fig. 6. Correlation between TDS and Cl^-.

of groundwater. In Fig. 6, it can be seen that Cl^- concentration increases with the increase of TDS, indicating that the groundwater is definitely affected by evaporation.

4.1.4.2. Mixing effect. The mixing effect is the effect of mixture of different kinds of water, resulting the final hydrochemical composition different from the original ones. The shallow groundwater of

study area, on the one hand is recharge by atmospheric precipitation, on the other hand, hydraulic connection with surface water provides channel to exchange each other. Therefore, mixing effect plays an important role in the initial hydrochemical compositions of groundwater.

4.1.4.3. Cation exchange and adsorption. Cation exchange and adsorption denotes the process of particle release of a certain media into groundwater and its inverse process, the cations in groundwater will be absorbed by media. The most common cation exchange taking place in the groundwater system is that the calcium and magnesium ions are removed from the solution and the exchanger solid releases sodium ions to replace the removed calcium and magnesium ions, which is expressed as:

$$Ca^{2+} + HCO_3^- + 2NaX \rightarrow 2Na^+ + HCO_3 + CaX_2$$

$$Mg^{2+} + HCO_3^- + 2NaX \rightarrow 2Na^+ + HCO_3 + MgX_2$$
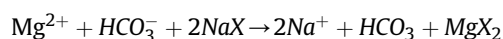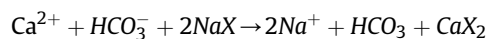
The (Na^+-Cl^-) versus ($HCO_3^- + SO_4^{2-} - Mg^{2+} - Ca^{2+}$) ratio has often used to identify the mechanisms for acquiring cation exchange and adsorption (An et al., 2012). If there is cation exchange and adsorption, the point is close to the 1:1 line. A high correlation ($R^2 = 0.768$) was observed in Fig. 7, indicating that there are different degrees of cation exchange adsorption in study area.
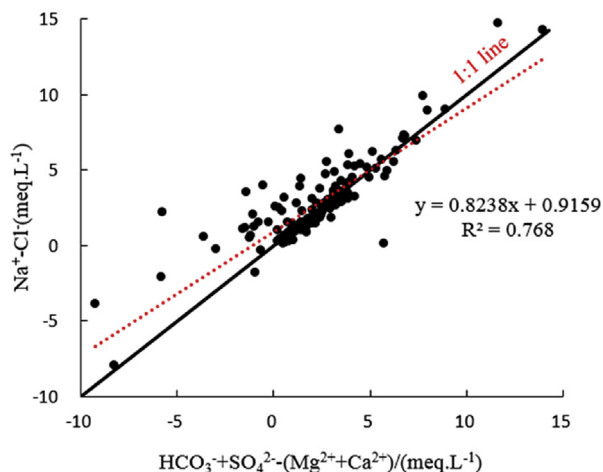
Fig. 7. $HCO_3^- + SO_4^{2-} - Mg^{2+} - Ca^{2+}$ versus $Na^+ - Cl^-$.

4.1.4.4. Anthropogenic activity. The impact of anthropogenic activities on the shallow groundwater components of the study area mainly includes the water diversion project, over exploitation, coal mining and agricultural cultivations, etc. These activities change the conditions of groundwater recharge and discharge, and have a complex effect on the leaching, mixing, and the cation exchange and adsorption.

In summary, the prevailing groundwater chemistry in the study area is the result of leaching, evaporation and concentration, mixing, cation exchange adsorption and anthropogenic induced activities. Silicate minerals such as calcite, dolomite are the most important dissolved substances, followed by the dissolution of gypsum.

4.1.5. Principal component analysis

Principal component analysis is multivariate statistical method to study the correlation between a set of variables (Xu and Xu, 2006). In order to investigate the role of each variable and meanwhile to simplify the original data structure, principal component analysis is used to extract principal components from the original dataset. In this paper, PCA was applied to chemical data to analyze the principal factors corresponding to the different processes that control water chemistry and sources of variation in the data. Principal component analysis was carried out with the help of SPSS software package to extract the factors (Sun, 2007). KMO (Kaiser-Meyer-Olkin) Measure of Sampling Adequacy (MSA) is generated in SPSS and is often used to determine if a dataset is "appropriate" for factor analysis, in this study, a KMO value of 0.65 was obtained, so the hydrochemical data is suitable to perform PCA. The size of the contribution rate of factor variance reflects the influence degree of the chemical characteristics of aquifer (Sun and Xing, 2010). In this paper, component's loadings larger than 0.7 was taken into consideration in the interpretation of geochemical processes. In other words, the most significant components represented by high loadings have been taken into consideration in evaluating the

contributions influencing chemical composition of groundwater. Factors with eigenvalues larger than 1 were taken into account. Table 2 summarizes the extraction sums of squared loadings and its eigenvalues and percent of variance contributed. It can be seen that the four most significant factors were generated, explaining about 78.85% of total variance of the data set, which indicates that the four factors can reflect the majority of the groundwater chemistry. The rotated component matrix is presented in Table 3, and the PCA loadings for parameters are visually illustrated in Fig. 8.

The variance contribution rate of the factor 1 is 42.10%, which is mainly composed of TDS, Mg^{2+}, Na^+, SO_4^{2-} and Cl^-. The sodium of water is mainly governed by the dissociation of halite and nitrate; Concentration of Cl^- may be considered as a result of the dissociation of halite. Sulfate and magnesium ions are partly derived from gypsum and human pollution.

Factor 2 explains 17.18% of the total variance and shows negative loading for pH and positive loading for Ca^{2+}. The pH ranges from 7.14 to 8.32, indicating a weakly alkaline environment, which may be caused by the leaching of dissolved constituents into the groundwater. The concentration of calcium of study area mainly dissolved carbonates. Therefore, the factor 2 reflects the leaching reaction in the weak alkaline geochemical background.

Factor 3 has a total variance of 10.43% with high loadings for HCO_3^- and NO_3^-. The higher loading of NO_3^- can be attributed to agricultural activities such as fertilizers, animal waste, crop residues and mineralization of soil organic nitrate and on the other hand non-agricultural sources such as septic tanks, effluents containing nitrogen discharged from industries. Bicarbonate commonly originates from dissolution of carbonate (Fadoua et al., 2011). Thus, factor 3 mainly reflects the impacts of the dissolution of carbonate minerals and human activities on the chemical composition of the shallow groundwater.

Factor 4 contributes 9.14% to the total variance with loading of NH_4^+ and COD. NH_4^+ is mainly derived from the utilization of nitrogen fertilizer, while COD stands for organic pollutants, which accounts for the higher loading of calcium in factor 4.

4.2. Groundwater quality assessment

4.2.1. Single factor analysis method

Understanding the groundwater quality is important as it is the main factor determining its suitability for drinking, domestic, agricultural, and industrial purposes (Subramani et al., 2005; Crévecoeur et al., 2011).

Two methods, single factor and set pair methods are applied to groundwater quality assessment. Single factor method was firstly used to determine the ions with significant impacts on groundwater quality, which were chosen as the evaluation index in set pair evaluation method. Finally, TDS (total salinity), Cl^-, TH (total

Table 2
Extraction sums of squared loadings.

Component	Total	% of variance	Cumulative %
1	5.47	42.10	42.10
2	2.23	17.18	59.26
3	1.36	10.43	69.71
4	1.12	9.14	78.85

Table 3
Rotated component matrix.

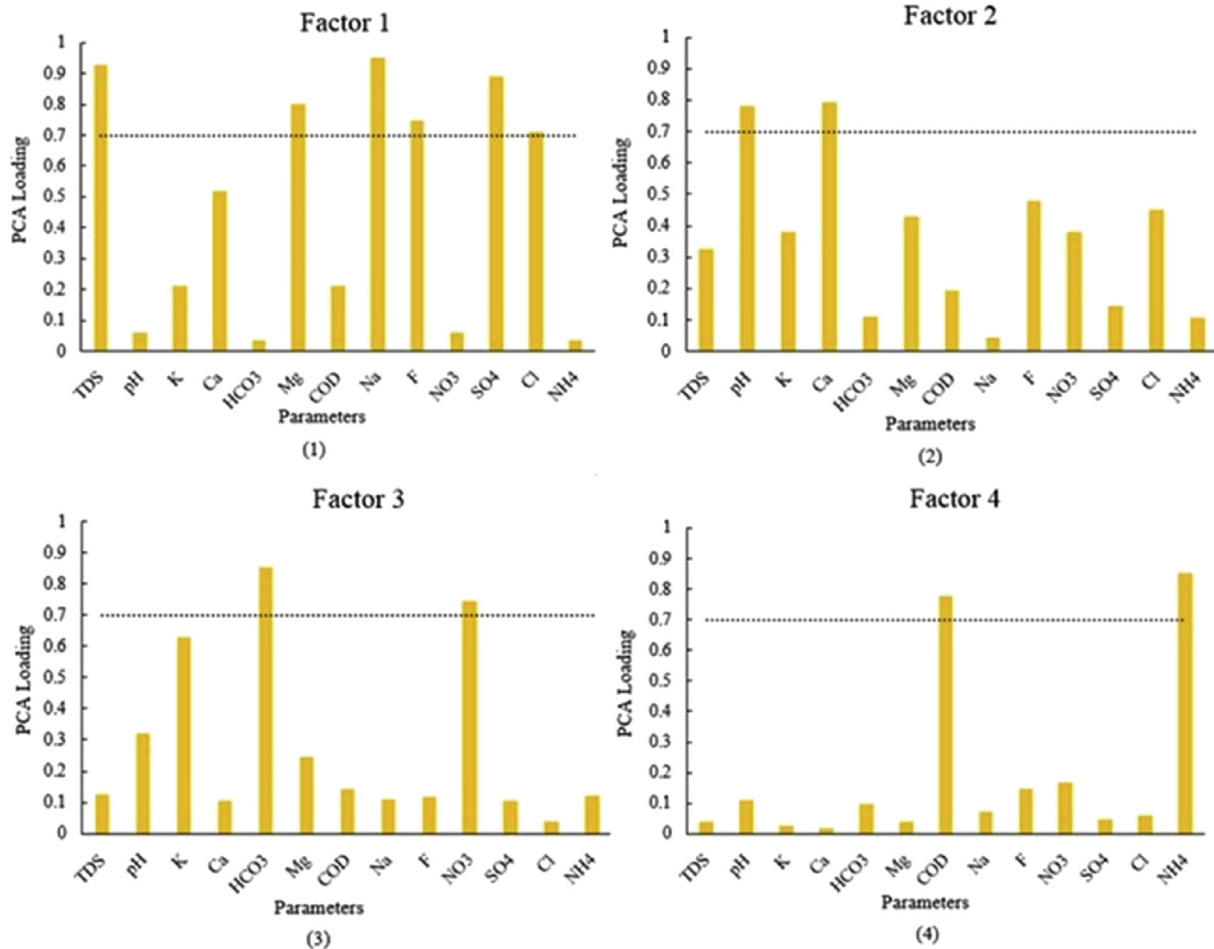| Parameter	Factor 1	Factor 2	Factor 3	Factor 4
TDS	0.925	0.322	0.121	0.035
PH	−0.057	−0.778	−0.319	−0.106
K^+	0.209	0.378	0.625	0.026
Ca^{2+}	0.516	0.790	0.100	−0.017
HCO_3^-	−0.035	−0.108	0.850	0.093
Mg^{2+}	0.798	0.425	0.242	0.038
COD	0.208	0.193	0.141	0.776
Na^+	0.952	−0.043	0.105	0.070
NO_3^-	0.060	0.379	0.743	−0.165
SO_4^{2-}	0.890	0.142	−0.103	0.045
Cl^-	0.707	0.448	−0.035	0.058
NH_4^+	−0.032	−0.102	−0.118	0.851

Fig. 8. PCA loading of four factors.

hardness), SO_4^{2-}, NO_3^-, NH_4^+, F^- and COD are selected as the evaluation index of the single factor analysis method. The regulation "groundwater quality standard" DZ/T 0209-2015 (Ministry of Land and Resources of P. R. China, 2015), which was promulgated in 2015, is adopted as the evaluation standard (Table 4); the evaluation results of each parameter and its proportion are summarized in Table 5. It can be seen from Table 5 that the highest proportion of Cl^-, F^- and COD ions in Excellent class accounts for 66.67%, 87.33% and 94%, respectively; The proportion of TDS, Cl^- and SO_4^{2-} ions in Good class is relatively high; The number of TDS, NO_3^- and NH_4^+ ions appeared more frequently in Permissible class; TDS, TH, NO_3^- and F^- presents a high proportion in Doubtful class, most part of TH and NO_3^- ions were categorized into Unsuitable class. Considering the above analysis, finally TDS, TH, SO_4^{2-}, NO_3^-, NH_4^+ and F^- are selected as the comprehensive evaluation index.

Table 4
Groundwater quality standard.

Index	I	II	III	IV	V
TDS	≤ 300	≤ 500	≤ 1000	≤ 2000	>2000
Cl^-	≤ 50	≤ 150	≤ 250	≤ 350	>350
TH	≤ 150	≤ 300	≤ 450	≤ 650	>650
SO_4^{2-}	≤ 50	≤ 150	≤ 250	≤ 350	>350
NO_3^-	≤ 2	≤ 5	≤ 20	≤ 30	>30
NH_4^+	≤ 0.02	≤ 0.1	≤ 0.5	≤ 1.5	>1.5
F^-	≤ 1	≤ 1	≤ 1	≤ 2	>2
COD	≤ 1	≤ 2	≤ 3	≤ 10	>10

Table 5
Results of single factor analysis method.

Index	I		II		III		IV		V	
	No.	Per (%)	No.	Per (%)	No.	Per (%)	No.	Per (%)	No.	Per (%)
TDS	26	16.77	49	32.67	53	35.33	19	12.67	3	2.00
Cl^-	100	66.67	34	22.67	9	6.00	1	0.67	6	4.00
TH	0	0.00	24	16.00	34	22.67	16	10.67	76	50.67
SO_4^{2-}	51	34.00	73	48.67	13	8.67	8	5.33	5	3.33
NO_3^-	7	4.67	9	6.00	68	45.33	17	11.33	49	32.67
NH_4^+	35	22.67	0	0.00	116	77.33	0	0.00	0	0.00
F^-	131	87.33	0	0.00	0	0.00	16	10.67	3	2.00
COD	141	94.00	13	8.67	0	0.00	1	0.67	0	0.00

Per, percentage; No., Sample Number; I,excellent; II, good; III, Permissible; IV, Doubtful; V, Unsuitable.

4.2.2. Set pair evaluation method

Set pair analysis (SPA) was initially proposed by Zhao (Zhao and Xuan, 1996), the theory of SPA is to construct two relative sets in an uncertainty system, and connection degree of the set pair can be established according to the identity, discrepancy and contrary. The application of SPA in groundwater quality assessment is to define a index and its corresponding standard as two assembly, namely a set pair. The essence of groundwater quality assessment is to compare the similarity between two objects. If they are similar, they will be classified into one class, if not, they will be classified into different classes.

In order to perform groundwater quality assessment with SPA method, a set pair must be made by putting the concentration of

each index and water quality standards together first. Then, the connection degree between each index of each monitoring sample and standards must be calculated. Then the average connection degree of each monitoring sample can be obtained. Subsequently groundwater quality class can be determined.

If the index is in the range of standard limit, the connection degree is set as 1; If not, the connection degree is considered to be −1; If in the adjacent standard level, that is, the simplified and improved the method to determine the degree of the following:

(1) According to the 5 level classification of the single factor index in the groundwater quality standard, the 5 element correlation degree is employed to depict the groundwater quality grade, it is expressed as:

$$\mu = a + bi + cj + dk + el$$

where, a, b, c, d, e represents the connection component between the samples and the water class and satisfies the normalization condition, $a + b + c + d + e = 1$.

(2) The connection degree between each evaluation index and evaluation classification standard is expressed as:

$$\mu_{jk} = \begin{cases} 1 + 0i + 0j + 0k + 0l & x \in [0, \ S_1] \\ \dfrac{S_2 - x}{S_2 - S_1} + \dfrac{x - S_1}{S_2 - S_1}i + 0j + 0k + 0l & x \in [S_1, \ S_2] \\ 0 + \dfrac{S_3 - x}{S_3 - S_2}i + \dfrac{x - S_2}{S_3 - S_2}j + 0k + 0l & x \in [S_2, \ S_3] \\ 0 + 0i + \dfrac{S_4 - x}{S_4 - S_3}j + \dfrac{x - S_3}{S_4 - S_3}k + 0l & x \in [S_3, \ S_4] \\ 0 + 0i + 0j + 0k + el & x \in [S_4, \ +\infty] \end{cases}$$

where, S_1, S_2, S_3, S_4 represents the upper threshold of grade I, II, III, IV grade, respectively, also S_4 is the lower threshold of V-grade standard; x is the actual monitoring value for various index.

(3) The weight of each index is determined by the entropy weight method,

$$\omega_j = (1 - H_j) \left/ \left(n - \sum_{j=1}^{n} H_j \right) \right.$$

$$\sum_{j=1}^{n} \omega_j = 1$$

(4) The formula for calculating the weighted average connection degree is:

$$\mu_k = \sum_{j=1}^{n} \omega_j \times \mu_{jk}$$

(5) The maximum weighted average connection degree is the final evaluation grade of the sample, which is calculated with $\delta = \mu_{k(\max)}$.

The TDS, TH, SO_4^{2-}, NO_3^-, NH_4^+ and F^- affecting most the groundwater quality obtained from single factor evaluation results, were selected as evaluation.

Fig. 9 demonstrates that the overall groundwater quality in the study area is not optimistic, excellent class hardly was observed, and most samples belong to permissible, doubtful and unsuitable classes. In general, excellent and good classes, which are suitable for various purposes, accounted for 12.90% of the study area; Permissible water, which is suitable for centralized production of drinking water and for industrial and agricultural purposes, accounts for 29.03% of. Unsuitable class, unfit for drinking water and can be considered as doubtful water of drinking water after proper treatment process, the doubtful water accounts for 58.065% of the survey area, mainly distributed in the surroundings of the study area.

5. Conclusions

The conventional hydrogeochemical techniques and statistical methods are applied to the hydrochemical dataset to provide insights for determining the hydrochemical processes controlling groundwater compositions in the southeastern part of Ordos Basin. The dominant cations in the area show an order of $Ca^{2+} > Mg^{2+} > Na^+ + K^+$ in terms of its abundance, and that of anion is $HCO_3^- > Cl^- > SO_4^{2-}$. Interpretation of hydrochemical analysis revealed that the major hydrochemical facies are $HCO_3 - Mg \cdot Ca \cdot Na$ and $HCO_3 - Mg \cdot Ca \cdot Na$ types in the study area.

Compositional relations have been employed to investigate the origins of solutes and confirm the predominant hydrogeochemical processes responsible for the various ions in the groundwater. The results revealed that leaching effect, evaporation condensation, mixing effect, cation exchange and adsorption and human activity are the dominant factors affecting the major ion compositions in the study area. The hydrochemical facies are interpreted as the dissolution of carbonates, silicates and halite.

The principle component analysis suggests processes responsible for hydrochemical characteristics of groundwater in the study area are anthropogenic activities such as fertilizer usage, water
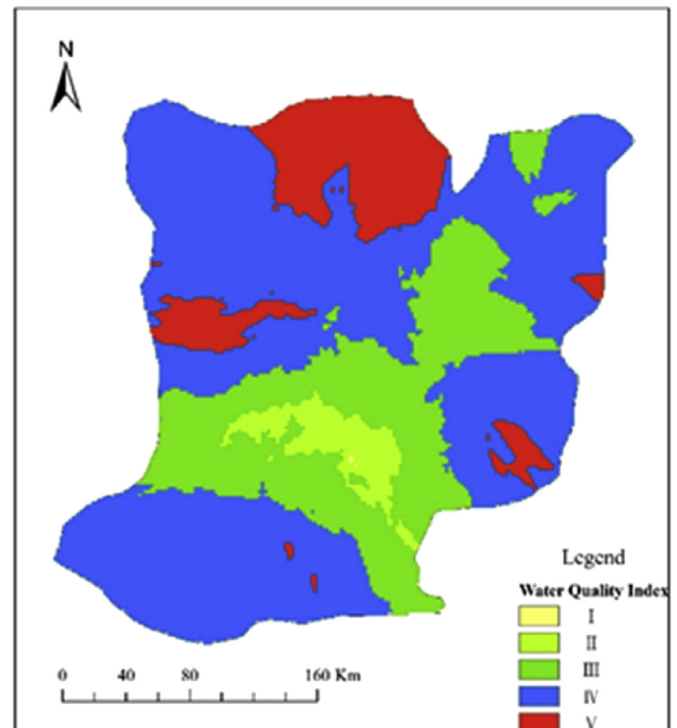

Fig. 9. Spatial distribution of groundwater quality index. I-excellent; II-good; III-Permissible; IV-Doubtful; V-Unsuitable.

pollution from industrial discharge and natural processes as geological effects and seasonal effects. Groundwater assessments results obtained from set pair evaluation method indicate that most of the samples are categorized into good marginal class. These results are insightful to understand the hydrogeochemical process which control the constitutes of groundwater, hydrochemical facies and groundwater quality in this arid area. The integrated methodology applied in this study have proven to be potential for investigating the groundwater chemistry in other areas.

Acknowledgments

References

An, L., et al., 2012. Hydrochemical characteristics and formation mechanism of shallow groundwater in the Yellow River delta. Environ. Sci. J. 33 (2), 370—378.

Cerling, T.E., Pederson, B.L., Damm, K.L.V., 1989. Sodium—calcium ion exchange in the weathering of shales: implications for global weathering budgets. Geol. J. 17 (6), 552—554.

Chang, J., Wang, G., 2010. Major ions chemistry of groundwater in the arid region of Zhangye Basin, northwestern China. Environ. Earth Sci. J. 61 (3), 539—548.

Crévecoeur, S., et al., 2011. Groundwater quality assessment of one former industrial site in Belgium using a TRIAD-like approach. Environ. Pollut. 159, 2461—2466.

Dong, W., et al., 2008. Study on distribution law of TDS and main ion concentration in groundwater in the Ordos Cretaceous Artesian Basin. Hydrogeol. Eng. Geol. J. (4), 11—15.

Fadoua, H.A., et al., 2011. Hydrogeochemical characteristics and asessment of drining water quality in Zeuss-Koutine aquifer, southeastern Tunisia. Environ. Monit. Assess. J. 174 (1), 283—298.

Fianko, Joseph Richmond, et al., 2010. The hydrogeochemistry of groundwater in the Densu river Basin Ghana. Environ. Monit. Assess. J. 167, 663—674.

Fisher, R.S., Mulican, W.F., 1997. Hydrochemical evolution of sodium-sulphate and sodium-chloride groundwater beneath the Northern Chihuahuan desert Trans-Pecos, Texas, USA. Hydrogeol. J. 10 (4), 455—474.

Ganyaglo, Samuel Y., 2012. Preliminary groundwater quality assessment in the central region of Ghana. Environ. Earth Sci. 66, 573—587.

Hong, Y., 2012. Analysis on Temporal & Spatial Variation about Groundwater Chemistry in the Lower Reaches of Tarim River. East China Normal University, Shang Hai.

Hou, G., et al., 2006. Groundwater system in Ordos cretaceous Artisan Basin. J. Jilin Univ. J. 36 (3), 391—398.

Jeevanandam, M., Kannan, R., Srinivasalu, S., Rammohan, V., 2007. Hydro-geochemistry and groundwater quality assessment of lower part of the pon-naiyar river basin, Cuddalore District, South India. Environ. Monit. Assess. 132, 263—274.

Kumar, S.K., et al., 2009. Assessment of groundwater quality and hydro-geochemistry of Manimuktha river basin, Tamil Nadia. Environ. Monit. Assess. J. 159, 341—351.

Kumar, P.J.S., Elango, L., James, E.J., 2014. Assessment of hydrochemistry and groundwater quality in the coastal area of south Chennai. India. Arab. J. Geosci. 7 (7), 1—13.

Maya, A.L., Loucks, M.D., 1995. Solute and isotopic geochemistry and groundwater flow in the Central Wasatch Range, Utah. J. Hydrol. J. 172 (1), 31—59.

Meybeck, M., 1987. Global chemical weathering of surficial rocks estimated from river dissolved loads. Am. J. Sci. J. 287 (5), 401—428.

Ministry of Health of P. R. China, 2006. Standards for Drinking Water Quality (in Chinese).

Ministry of Land and Resources of P. R. China, 2015. Standard for Groundwater Quality DZ/T 0290-2015. Geological Press (in Chinese).

Nickson, R.T., McArthur, J.M., et al., 2005. Arsenic and other drinking water quality issues, Muzaffargarh District, Pakistan. Appl. Geochem. J. 20, 55—68.

Purushotham, D., Prakash, M.R., Narsing Rao, A., 2011. Groundwater depletion and quality deterioration due to environmental impacts in Maheshwaram water-shed of R.R. district, AP (India). Environ. Earth Sci. 62 (8), 1707—1721.

Rao, S.N., 2008. Factors controlling the salinity in groundwater in parts of Guntur district, Andhra Pradesh, India. Environ. Monit. Assess. J. 138 (1—3), 327—341.

Reddy, A.G., Kumar Niranjan, K., 2010. Identification of the hydrogeochemical processes in groundwater using major ion chemistry: a case study of Penna-Chitravathi river basins in Southern India. Environ. Monit. Assess. J. 170 (1), 365—382.

Reuss, J.O., Johnson, D.W., 1986. Acid deposition and the acidification of soil and waters. Ecol. Stud. J. 2 (9), 285.

Shen, Z., 1993. Fundamentals of Hydrogeochemistry. Geological Publishing House, Beijing, pp. 71—78.

Su, Y., et al., 2009. A study of shallow groundwater quality distribution in the Ordos Cretaceous Artisan Basin based on GIS. Hydrogeol. Eng. Geol. J. 36 (l), 24—29.

Subramani, T., Elango, L., Elango, L., Damodarasamy, S.R., 2005. Groundwater quality and its suitability for drinking and agricultural use in Chithar River Basin, Tamil Nadu, India. Environ. Geol. J. 47, 1099—1110.

Sun, B., 2007. Application of Multivariate Statistics Method into Research on Spatial Distribution Law of Hydrochemistry in Dusituhe Groundwater Systerm in Ordos Cretaceous Basin. Ji Lin University, Chang Chun, pp. 37—40.

Sun, B., Xing, L., 2010. Research on groundwater chemical characteristics in Urban areas in Jinan. China Rural Water Conservancy hydropower. J. 11, 33—40.

Tizro, T.A., Voudouris, K.S., 2008. Groundwater quality in the semi-arid region of the Chahardouly basin, West Iran. Hydrol. Process. J. 22 (16), 3066—3078.

Vengosh, A., Keren, R., 1996. Chemical modifications of groundwater contaminated by recharge of treated sewage effluent. J. Contam. Hydrology 23, 347—360.

Wen, X., et al., 2005. Hydrochemical characteristics and salinity of groundwater in the Ejina basin northwestern China. Environ. Geol. J. 48 (6), 665—675.

Xu, J., Xu, H., 2006. Data Statistical Analysis and SPSS Application. People's Posts and Telecommunications Press, Beijing, pp. 291—298.

Yang, Q., et al., 2016. Hydrochemical characterization and pollution sources identification of groundwater in Salawusu aquifer system of Ordos Basin, China. Environ. Pollut. 216, 340—349.

Zhao, K.Q., Xuan, A.L., 1996. Syst. Eng. 14 (1), 18—23, 72.