Invited paper

Hydrochemical characterization and pollution sources identification of groundwater in Salawusu aquifer system of Ordos Basin, China[☆]

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ABSTRACT

Ordos Basin is located in an arid and semi-arid region of northwestern China, which is the most important energy source bases in China. Salawusu Formation (Q_3 s) is one of the most important aquifer systems of Ordos Basin, which is adjacent to Jurassic coalfield areas. A large-scale exploitation of Jurassic coal resources over ten years results in series of influences to the coal minerals, such as exposed to the oxidation process and dissolution into the groundwater due to the precipitation infiltration. Therefore, how these processes impact groundwater quality is of great concerns. In this paper, the descriptive statistical method, Piper trilinear diagram, ratios of major ions and canonical correspondence analysis are employed to investigate the hydrochemical evolution, determine the possible sources of pollution processes, and assess the controls on groundwater compositions using the monitored data in 2004 and 2014 (before and after large-scale coal mining). Results showed that long-term exploration of coal resources do not result in serious groundwater pollution. The hydrochemical types changed from $HCO_3^- $-$CO_3^{2-}$ facies to SO_4^{2-}-Cl facies during 10 years. Groundwater hardness, nitrate and sulfate pollution were identified in 2014, which was most likely caused by agricultural activities.

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1. Introduction

Groundwater is a crucial source of fresh water throughout the world (Alley et al., 2002) Unfortunately, groundwater quality in the most area of the world, such as India, Korea, Greece, America, China, has deteriorated due to the increased human population and anthropogenic activities, various industrial and agricultural activities (Lambrakis, 1998; Zhang, 1998; Purushotham et al., 2011; Hosono et al., 2009; Li et al., 2014). In arid and semi-arid regions, groundwater is an essential part of the total water resources, and has important implications for the economic development (Subyani and Al-Ahmadi, 2010; Yin et al., 2011).

Ordos Basin, is located in arid and semi-arid region of northwestern China, is one of the essential energy and chemical bases of China with great potential for economic development. However, one of the main factors restraining economic development is the availability of water resources because this region is characterized with scarcity and uneven distribution of water resources, and groundwater is the main supplier for domestic, industrial and agricultural purposes. Salawusu Formation is the primary aquifer of the northern Ordos Basin, where groundwater is the important resource of water supply and also maintains the ecological environment of this area. Long-term and large-scale exploitation of mineral resources and rapid development of agricultural production have exerted potential impacts on shallow groundwater, ecological environment deterioration: aquifers or aquitard destruction, groundwater level decline, surface runoff decrease, spring cutoff, groundwater pollution, and so on. Therefore, with the rapid development of coal and oil industries and agriculture in the last decade, it's urgent to investigate groundwater quality variations of Salawusu aquifer system.

Assessment of groundwater quality is used for understanding its origin and mineralization process, also useful for exploring water-rock interaction and analyzing the environment questions of the area (Pathak, 2012; Schofield and Jankowski, 2004). The present study focuses on the main hydrochemical processes which would affect groundwater quality and hydrochemical types. The specific

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objectives include (I) confirm the hydrochemical types and the variation trend; (II) analyze the variation of water quality between 2004 and 2014 , and determine whether the groundwater quality meets the standard of drinking water; (III) understand water-rock interaction, groundwater mineralization process; (IV) determine the main pollution indicators and their formation processes.

2. Study area and methods

2.1. Location and characterization of study area

Ordos basin is located in northwestern China, encompassing Shaanxi Province, Gansu Province, Ningxia Province, Shanxi Province and Inner Mongolia. In geology tectonics. It is a large sedimentary basin superposed by Paleozoic and Mesozoic sediments, 640 km from north to south and 400 km from east to west, it covers approximately 275,000 square meters (Wang et al., 2002) . Climate: these are warm temperate continental monsoon climate, low precipitation, great evaporation, fragile ecological environment, obvious seasonal variations of precipitation and temperature, the average annual rainfall was 350–400 mm, and the annual mean evaporation was 2200–2800 mm. Surface water resources in Ordos basin are extremely deficient, groundwater account for 60% of the total water resources. Ordos basin has a vast territory, and is abundant in minerals resources, such as coal, petroleum, gas, coalbed methane, rock salt and so on. Coal, natural gas, and petroleum amounts more than 20% of the total reserves of China.

The study area is situated in the northeastern part of Ordos basin (Fig. 1), between 38° and 40°20′N and 109°and 111°E. The north district of the study area is desert plateau, and the south district is loess plateau. Groundwater system in the study area mainly includes Salawusu aquifer system, Jurassic-Carboniferous aquifer system, the Quaternary aquifer system, Cretaceous aquifer system, which are multilayered and heterogeneous. The main lithology in Salawusu Formation is fine sand, silty-fine sand, conglomeratic sandstones, with good sorting, high permeability, which is easily recharged by precipitation and difficult to collect surface runoff (Wang, 2008). The bottom of the Jurassic-Carboniferous clastic rock layer is much composed of sandstones and mudstone interbedding, which is rich with coal, petrol and other mineral resources.

2.2. Sampling and measurements

This study is a branch of "Investigating and Assessment of Groundwater Pollution of Ordos basin" project of China Geological Survey. Groundwater samples were collected from 84 active phreatic wells from June to September in 2014 and 123 samples were collected from hydrological geology and pollution investigation conducted in 2004. The survey chooses the representative sampling sites based on the overall state of groundwater quality and pollution obtained from previous studies. All of the water samples were collected from the wells in pre-cleaned, and were kept in colored glass bottles to remove stagnant water from the well and stored at 4 °C and then transferred. The in-situ monitored indexes include temperature, water temperature, pH, electrical conductivity, redox potential, dissolved oxygen, turbidity. Other 27 chemical parameters were analyzed in the laboratory, including total dissolved solids (TDS), total hard (TH), potassium permanganate index, nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), sulfate (SO_4^{2-}), and so on.

2.3. Analytical methods

The descriptive statistics method, Piper trilinear diagram, ratios
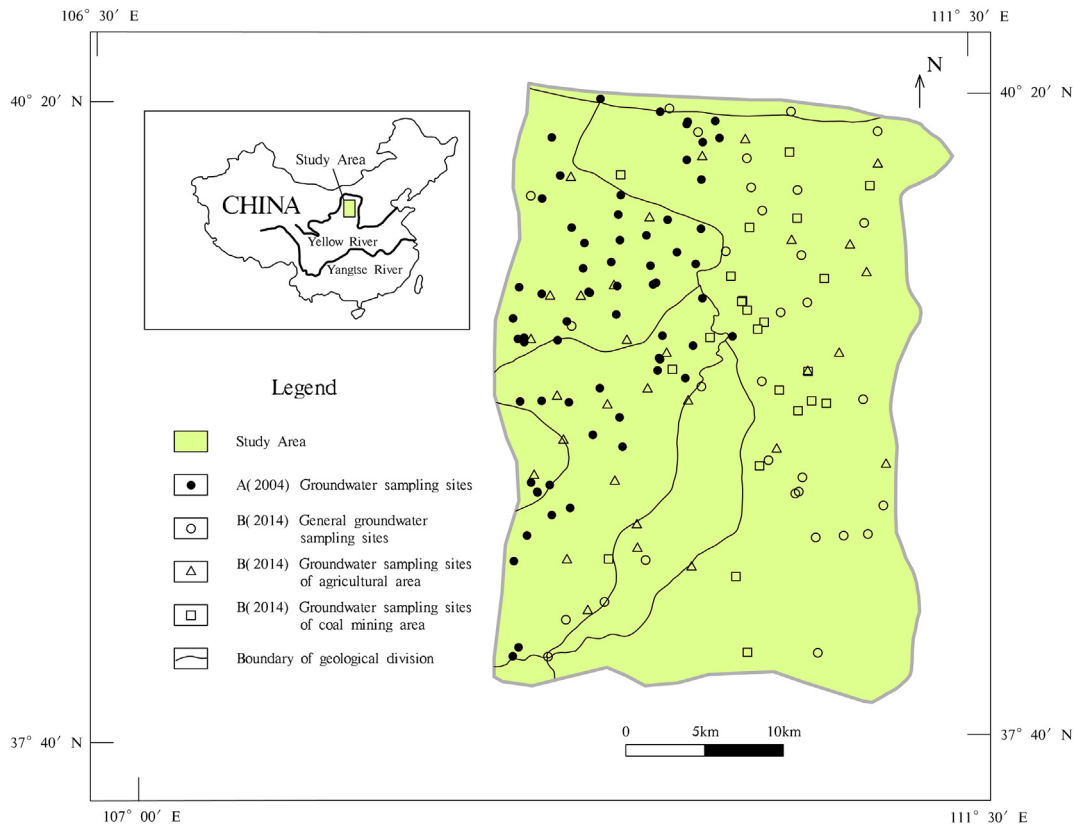
Fig. 1. Sampling location map of the study area.

of major ions and correspondence analysis are employed to evaluate the changes of groundwater quality during 10 years.

The groundwater is the main drinking water supply source of the study area, therefore, the results of descriptive statistics method should be evaluated and classified for hydrochemical parameters following the regulation of drinking water quality (WHO, 2011).

The Piper trilinear diagram (Piper, 1944) is one of the most useful graphical representations in groundwater quality studies and helps in understanding the geochemical of shallow groundwater (Purushotham et al., 2011). The geochemical evolution of groundwater can be understood by plotting the concentration of major cations and anions in the Piper trilinear diagram (Chidambaram et al., 2011). And it can reveal hydrochemical types and its evolution. The major advantage of this method is not influenced by artificial factor.

Ratios of major ions can be used to analyze concentration of different major elements and their interrelationship, and to understand and illustrate hydrogeochemical processes and the origin of the groundwater chemical composition (Kumar et al., 2014; Wang et al., 2014).

Correspondence analysis (CA) is a multivariate statistical analysis method for dissimilar variables, which is capable of revealing the internal relationships between samples and variables through a cross table formed by qualitative variables. According to CA principle, the eigen values of covariance matrix A of variate and variance of proportion were calculated. The patterns obtained are usually interpreted in relation to external data such as correlation coefficients between independent variables and ordination axes or with multiple regression of the ordination axes on independent variables (Legendre and Legendre, 1998; Angers et al., 1999). CA selects the top two factors with maximum variance as principle

factors axes, which have the highest resolution, calculates the factor loading values of R-type and Q-type, and then maps the factor loading projection plane graph. CA technique was applied to analyze water quality parameters exceeded quality standard, and to explore the major pollutants and pollution sources.

3. Results and discussions

3.1. Characteristics of groundwater quality

The nineteen water quality parameters selected in statistical analysis are pH, total dissolved solids (TDS), total hardness (TH), potassium (K^+), sodium (Na^+), calcium(Ca^{2+}), magnesium (Mg^{2+}), aluminum (Al^{3+}), manganese (Mn), iron (Fe), zinc (Zn), fluoride (F^-), bicarbonate (HCO_3^-), chloride(Cl^-), carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), nitrate(NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), which pH was dimensionless, other ionic concentrations' units were in mg/L. The software Office Excel 2013 and SPSS Statistics 19.0 were used for statistical analysis and correspondence analysis.

Groundwater quality characteristics are summarized in Table 1. By comparing the statistical data of 2004 (Group A) and 2014 (Group B), it can be observed that (i) the concentrations of groundwater major ions in both groups are similar, the major cation were Ca^{2+} and Mg^{2+} and the primary anion was HCO_3^-. The order of dominant cations is $Ca^{2+}>Na^+>Mg^{2+}>K^+$ in both two groups, and that of anions is $HCO_3^- \gg SO_4^{2-}NO_3^->Cl^->CO_3^{2-}$, indicating hydrochemical types of groundwater did not show great change; (ii) 14 of 19 parameters' concentration increased with different levels, and significant changes are found for Na^+, Ca^{2+},Cl^-, NO_3^-, SO_4^{2-}, HCO_3^-. The increment of anion concentration was more apparent, and the most remarkable anion is SO_4^{2-}, followed by HCO_3^- and NO_3^-. For cation, the average concentration of Na^+ and Ca^{2+} increased

Table 1
Comparison analysis of groundwater quality parameters between A (2004) and B (2014).

Parameter	WHO standards 2004	Ground water										Variation avg.
		A(2004)					B(2014)					
		Valid data	Min	Max	Avg.	S.D.	Valid data	Min	Max	Avg.	S.D.	
pH[*]	6.5−8.5	84	7.10	8.97	7.81	0.44	122	6.80	9.10	7.83	0.40	↑0.02
TDS[*]	500−1000	84	0	1062	364.44	**157.82**	122	128	1597	488.79	**284.85**	↑124.35
TH[*]	500	84	25	666	215.11	**80.54**	121	57.5	699	265.33	**137.01**	↑50.22
K^+	20	84	0.50	12.40	2.58	6.46	123	0.47	15.80	2.65	2.32	↑0.07
Na^{+}[*]	200	84	8.10	189.79	49.83	37.13	122	6.21	283.00	65.77	65.54	↑15.94
Ca^{2+}	100	84	7.84	147.29	50.71	20.61	123	7.33	194.00	67.57	39.46	↑16.86
Mg^{2+}	50	84	1.22	77.65	21.27	11.46	123	6.16	66.00	23.46	13.63	↑2.19
Al^{3+}	0.1−0.2	84	0.00	0.04	0.01	0.01	21	0.01	0.32	0.02	0.03	↑0.01
Mn	0.4	84	0.00	0.21	0.04	0.06	21	0.00	0.64	0.01	0.07	↓0.03
Fe[*]	0.3	84	0.00	0.25	0.02	0.84	67	0.00	0.007	0.01	0.01	↓0.01
Zn[*]	4	84	0.00	0.46	0.04	0.08	40	0.00	0.47	0.01	0.05	↓0.03
F^-	1.5	82	0.00	2.58	0.48	0.35	122	0.20	3.00	0.64	0.54	↑0.16
HCO_3^-	125−350	84	27.50	445.42	223.78	**68.90**	123	60.85	628.20	258.22	**101.40**	↑34.43
Cl^-[*]	250	84	3.50	194.99	35.50	33.87	123	1.81	233.30	45.35	54.67	↑9.85
CO_3^{2-}		84	0.09	36.31	3.55	6.36	123	0.05	26.16	1.75	3.75	↓1.80
SO_4^{2-}[*]	250	84	4.81	315.57	54.93	**59.46**	123	4.80	413.10	94.92	**94.20**	↑39.99
NO_3^-	50	78	0.00	228.59	26.32	**40.65**	122	0.00	900.00	46.58	**117.31**	↑20.26
NO_2^-	3	10	0.00	1.64	0.06	0.18	122	0.00	1.25	0.13	0.39	↑0.07
NH_4^+[*]	35	84	0.00	27.96	0.27	2.54	122	0.00	0.24	0.04	0.08	↓0.23

Note: [*]not of health concern at levels found in drinking-water.
The max. over standard, avg. with changing significantly, high S.D. are written in box, underline, bold fond respectively.

obviously. The standard deviations of TDS、TH、HCO_3^-、SO_4^{2-}、NO_3^- change greatly; (iii) the measured parameters of A and B are compared with Guidelines for drinking-water quality (WHO, 2011). Descriptive assessment of the drinking water quality on the basis of the measurements results according to the prescribed limits by WHO or other agency will give the results in form of linguistic term like 'desirable', 'acceptable' and 'not acceptable'. All the parameters' mean values met the standard, except for very few samples that cannot be drank directly and can be used for industrial water or agricultural water, the whole groundwater quality in the study area was acceptable. The maximum concentration of some indicators exceeded standard, such as TDS, TH, Na^+, Ca^{2+}, Mg^{2+}, Mn, F^- HCO_3^-, NO_3^- SO_4^{2-}, but TH, Na^+ and other parameters were not of health concern at levels found in drinking water.

3.2. Hydrochemical facies

As water flows through an aquifer, it assumes a characteristic chemical composition as a result of interaction with the surrounding rock and soil, the term "hydrochemical facies" is used to describe the bodies of groundwater in an aquifer, which is different from their chemical composition (Ravikumar and Somashekar, 2013). The Piper trilinear diagrams can summarize the main contrasts in hydrochemical composition among different water sources (Soulsby et al., 1998; Wang Rui et al., 2014). The diamond shaped field between the two triangles is used to represent the composition of water with respect to both cations and anions (Raju et al., 2009).

Piper diagrams of group A and group B are shown in Fig. 2. It can be seen that (i) the overall hydrochemistry is dominated by alkaline earth metal ions and weak acid, calcium and bicarbonate have much contribution to the hydrochemical compositions. The majority of the samples of both A and B belong to $HCO_3^- \cdot CO_3$-Ca·Mg type with low salinity; (ii) it can be observed that the plots of A are mainly concentrated in $HCO_3^- \cdot CO_3$-Ca·Mg field, but the plots of B are relatively scattered, indicating the hydrochemical type of the study area have changed to be complicative; (iii) it can be seen in Fig. 2a, 95 of the total 123 water samples fall in zone ①, $HCO_3^- \cdot CO_3$-Ca· Mg type, accounting for 77.24% of all, 13.01% of water samples falls in zone②, SO_4·Cl-Ca·Mg type, 1.62% of water samples falls in zone ③, SO_4·Cl-Na, and 8.13% of water samples falls in zone ④, $HCO_3^- \cdot CO_3$-Na type. Fig. 2b also shows that 69.05% of water samples falls in zone①, 11.905% of water samples falls in zone ② and zone ③, respectively, and 7.14% of water samples falls in zone ④. Based on the allocation proportions, one can draw a conclusion that types of $HCO_3^- \cdot CO_3$-Ca·Mg, SO_4·Cl- Ca·Mg, $HCO_3^- \cdot CO_3$-Na decreased, and SO_4·Cl-Na type increased. The two triangles of Piper trilinear diagrams (blue circle) deomonstrate the increased concentrations of Na^+ and K^+, and hydrochemical type transferred from bicarbonate and carbonate types to sulfate and chloride types. (iv) in 2014 (Fig. 2b), samples of agricultural area fall in zone ①, samples of coal mining area spread into zone ② and zone ③,, indicating hydrochemical types of coal mining area's samples are more complex.

Comparison between Fig. 2a and Fig. 2b suggests that groundwater hydrochemical types have changed before and after 10 years, which was likely caused by evaporation and concentration or cation-exchange and adsorption.

Evaporation is the major discharge pattern of groundwater due to dry climate, low-lying territory and shallow buried depth of groundwater in the study area. There the groundwater evaporates and calcium hydrogen carbonate and magnesium bicarbonate are deposited, so sulfate and sodium gradually become the main components in groundwater. Groundwater flow and dissolved

action would create the possibility of ion-exchange reactions, thus the concentration of Ca^{2+} is reduced and the concentration of Na^+ is increased. The increased concentration of Sulfate might be related to the dissolution of gypsum ($CaSO_4 \cdot 2H_2O$) or other deposits of sulfate minerals. Also previous study suggested that groundwater evolution of Ordos desert plateau was affected by the dissolving of gypsum and other sulfate minerals (Wu et al., 2011). Moreover, there are coal strata in the study area, which are abundant in pyrite. Percolation of groundwater through the coal strata will result in the dissolution of pyrite, this is another reason for large concentration of sulfate in groundwater.

3.3. Relationships among major ions

In order to investigate the possible origin of the each major element involved in groundwater chemical interaction and the geochemical process which controls the groundwater chemistry (Moussa et al., 2009), concentration of Na^+ versus Cl^-, Ca^{2+} versus SO_4^{2-}, Mg^{2+} versus SO_4^{2-} and $(Ca^{2+}+Mg^{2+})-(SO_4^{2-}+ HCO_3^-)$ versus $(Na^++ K^+- Cl^-)$ are illustrated in Fig. 3.

Most diagnostic methods for distinguishing among the probable sources of Na^+ and Cl^- in contaminated water samples appeared to be ratios of halides (Br^-, Cl^-, I^-) plotted against their own concentrations, total N, and Na^+ (Panno et al., 2006). Cl^- is treated as conservative solute without retardation, because it's almost unaffected by physical and chemical changes, and independent of other ions. The results shows that Cl^- concentration increases with increasing of TDS concentration (Shen, 1993). Cl^- is difficult to be absorbed by plants, bacteria or surface particles of soil, and the solubility of chlorine in water is high. The high concentration of Cl^- in arid area is the result of evaporation, which can be used as an indicator to detect the mineralization degree of groundwater. In order to determine whether evaporation and concentration played a dominant role in the hydrochemical types, Cl^- & TDS relationship was first established. It can be seen in Fig. 3a that Cl^- is positively correlated with TDS in most of samples, indicating that evaporation and concentration are salinization processes of groundwater in the study area.

Chloride in groundwater originates from the dissolution of disseminated halite in fine-grained sediments (García et al., 2001). Na^+-Cl^- ratio diagram can determine whether Na^+ and Cl^- are originated from the same source and explain why the groundwater type changed to Cl^--Na^+ type. The ratio of Na^+ versus Cl^- will be 1 if halite dissolution is dominant (Meybeck, 1987). In Fig. 3b, the linear increase of Na^+ with Cl^-, suggested that halite dissolved intensely in groundwater. The dissolution of halite in water releases equal concentration of Na^+ and Cl^- into the solution. Therefore, the samples above 1:1 line indicated the dissolution of halite is not the only source of Na^+. The $\gamma Na/\gamma Cl$ ratio is considered as one of the most important indicator in determining the origin of groundwater, close to 1 indicating the groundwater flows from the bottom of halite. The samples whose $\gamma Na/\gamma Cl$ exceeding 1 accounts for 93.5% and 95.24% for A's samples and B's samples, respectively, further indicating that Na^+ has other source, which was likely caused by ion-exchange reactions.

Moreover, SO_4^{2-}/Ca^{2+}, SO_4^{2-}/Mg^{2+} were used to identify the source of Ca^{2+}, Mg^{2+} and SO_4^{2-}. A poor correlation between Ca^{2+} and SO_4^{2-} was observed in Fig. 3c, suggesting that the solution of gypsum and anhydrite was not the cause of increasing SO_4^{2-}. However, a slightly better relationship exists between Mg^{2+} & SO_4^{2-} than Ca^{2+} & SO_4^{2-}. The contributions of evaporitic salts are shown by the positive correlations between $MgSO_4$ (Adams et al., 2001). It is therefore inferred that Mg^{2+} and SO_4^{2-} are mostly originated from the $MgSO_4$ fertilizer (Gi-Tak et al., 2004).

Bivariate plots of $(Ca^{2+}+Mg^{2+})-(SO_4^{2-}+ HCO_3^-)$ versus $(Na^+ +$
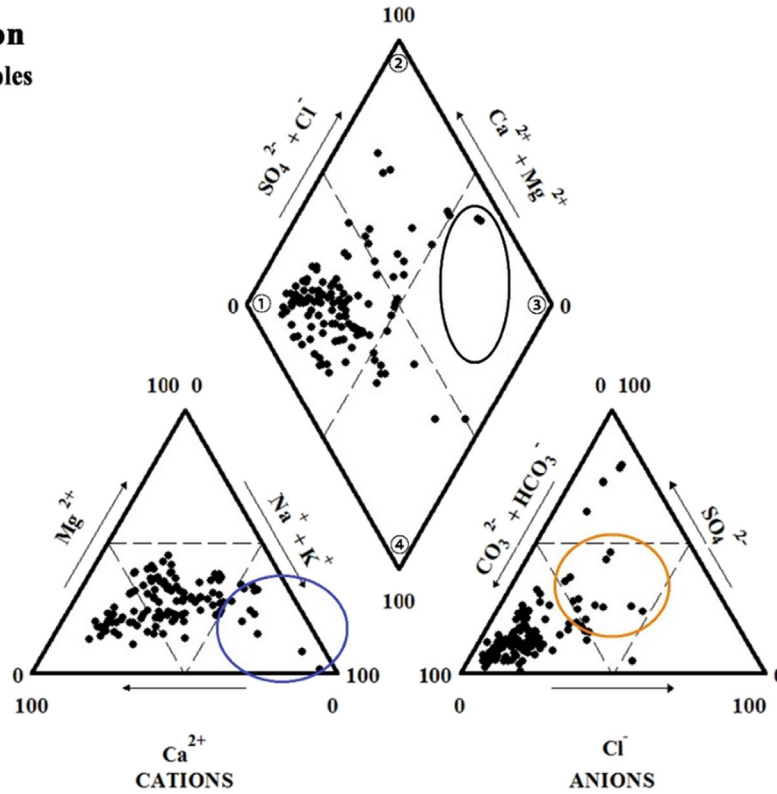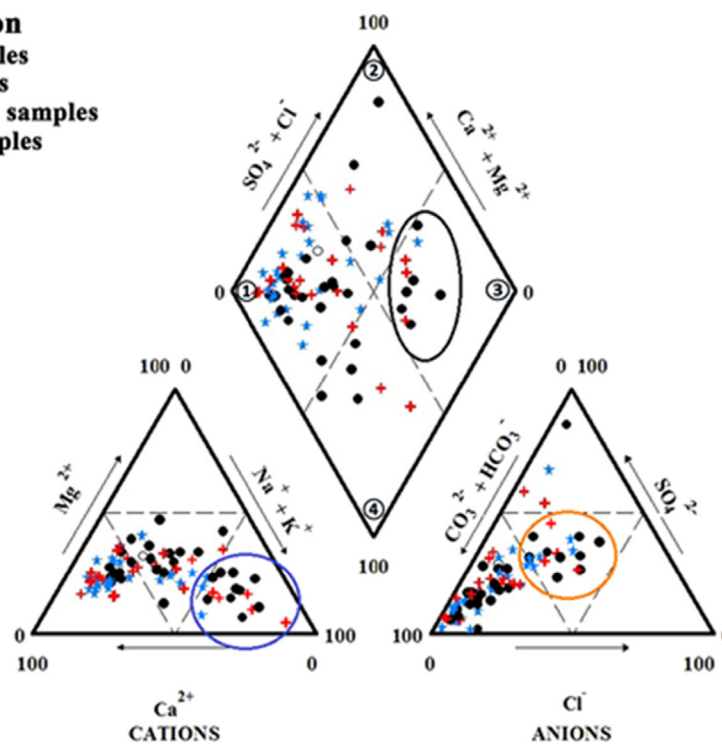
Fig. 2. Chemical facies of the groundwater of the study area. ①calcium magnesium bicarbonate; ②Calcium magnesium sulfate chloride; ③sodium sulfate chloride; ④sodium bicarbonate.

$K^+- Cl^-$) is shown in Fig. 4. In the absence of this exchange all data should be close to the origin (McLean et al., 2000). The pictorial evidence for cation exchange is given by the linear relationship between $(Ca^{2+}+Mg^{2+})-(SO_4^{2-}\ HCO_3^-)$ and $(Na^+ + K^+ - Cl^-)$ with the slope equals to -1 (García et al., 2001).

The linear regression equation of the relationship between $(Ca^{2+}+Mg^{2+})-(SO_4^{2-}+ HCO_3^-)$ and $(Na^+ + K^+ - Cl^-)$ was established to discover whether ion-exchange exists or not.
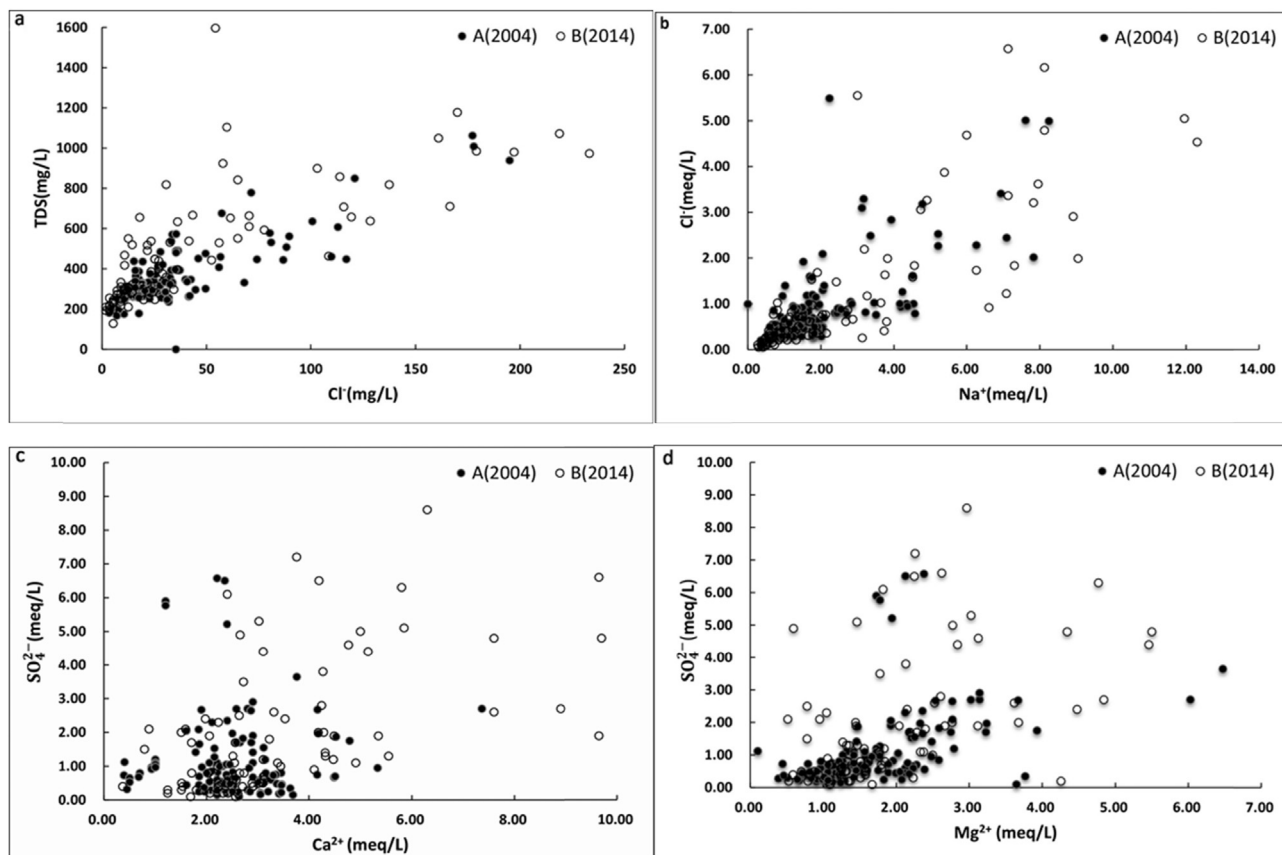
Fig. 3. Relationships between major elements.

$$A: Y = -0.879X + 0.563 \quad R^2 = 0.593$$

$$B: Y = -1.087X + 0.917 \quad R^2 = 0.764$$

The slope of B (2014) is −1.087, close to −1, indicating the ion exchange in groundwater of the study area is subject to cation exchange in 2014.

3.4. Groundwater pollution analysis

The serial numbers of sampling points exceeding WHO regulations are given in Table 2. It is observed that the number of samples in 2014 is larger than those in 2004, 40.48% of the B's samples contained at least one parameter beyond WHO standards, and that of A's samples was 16.26%. The parameters beyond WHO standards are prominent on HCO_3^- and NO_3^-. So groundwater quality has been worsen recent years, which was consistent with the previous study performed by Wang (2006), who stressed that groundwater pollution caused by nitrate has become a threat in recent years in Ordos Basin.

3.5. Correspondence analysis

The results of correspondence analysis of A(2004) and B(2014) data set using factor load matrix (Table 3) are plotted in Fig. 5, it shows that sampling locations and parameters have similar distribution.

Four main factors were chosen from the factor loading matrix. The first principle factor axis plays a vital role in groundwater pollution analysis of the study area. It can be seen the highest absolute value of F1 and F2 axis were SO_4^{2-} and NO_3^-, so F1 can reflect the content of SO_4^{2-} and NO_3^- in 2004 and 2014, respectively. Thus water samples with higher sulfate and nitrate content are closer to the positive F1 axis in 2004 and 2014. The second main factor axis can also evaluate water quality with less effect than F1. F2 axis can reflect the impact of HCO_3^- and SO_4^{2-} content to groundwater quality. Na^+, F^-, Mg^{2+}, Mn and other parameters are located in the center of F1 and F2 axis, with lower factor loadings, so these parameters are not the major indicators of water quality in the study area. The samples collected in 2004 (Fig. 5a) are close to the coordinate axis, indicating the groundwater was of good quality in 2004. But it can be seen in Fig. 5b that NO_3^-, the major factor of F1 axis, is closely related to the samples collected from agricultural mining area. And TDS, SO_4^{2-} and Na^+ are closely related to the samples collected in coal mining area. Therefore, it can be inferred that nitrate pollution may be linked to agricultural activity and higher sulfate content may be related to coal mining. Sulfate is the main constituent of dissolving salt, and exists in Glauber's salt and gypsum forms in the Cretaceous strata. The soluble salts in the aquifers of this area include sulfate (Glauber's salt and gypsum) and sulfide, and the lower strata is rich in oil and natural gas. So the sulfate of groundwater mainly originates from Glauber's salt and gypsum, followed by the sulfides from stratum, and then the organic sulfur (Yang et al., 2008).

3.5.1. The origin of groundwater contaminants

The results of correspondence analysis and descriptive statistics method show that the nitrate pollution and groundwater hardening has occurred in the study area during 2004—2014. Previous
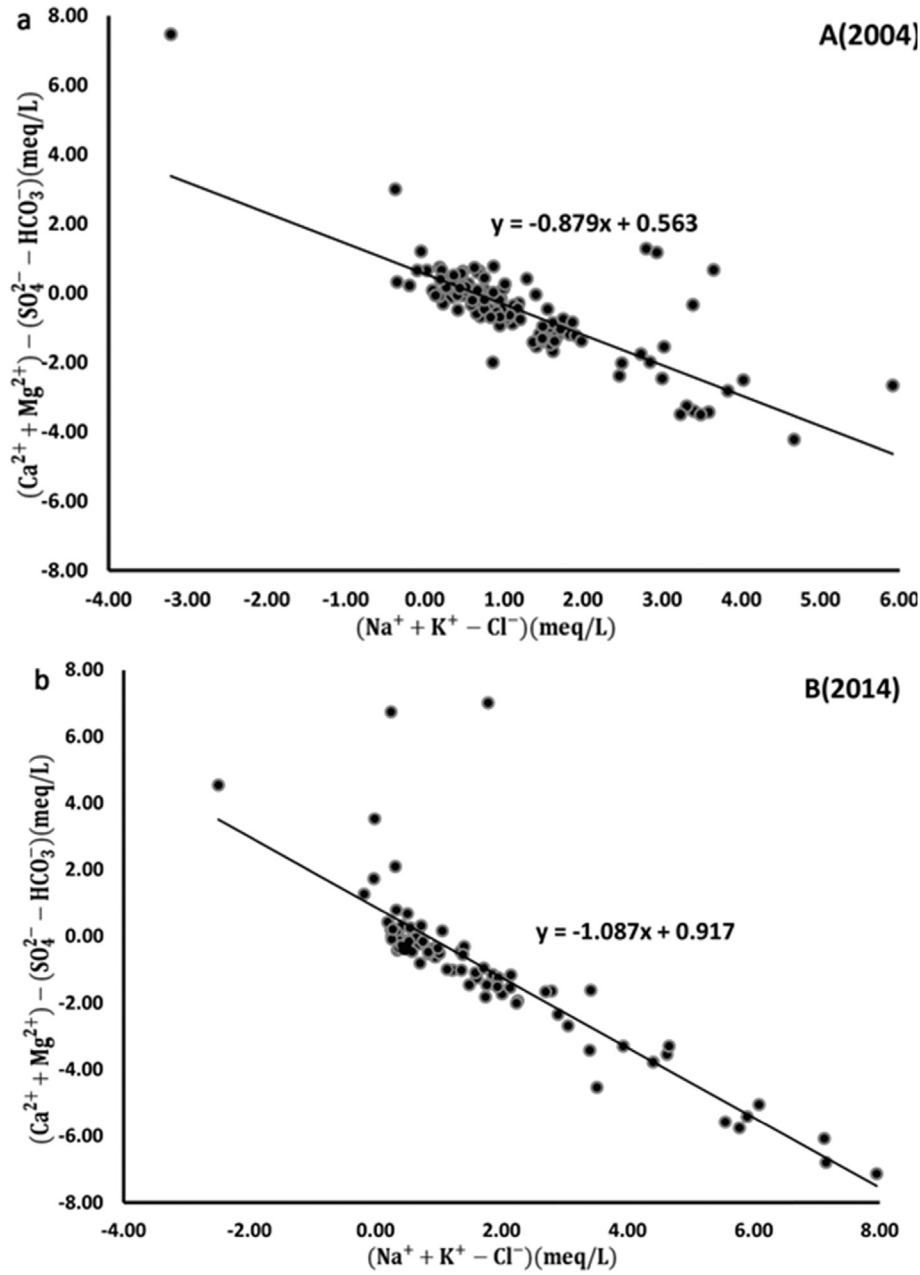
Fig. 4. Bivariate plot of $(Ca^{2+}+Mg^{2+})-(SO_4^{2-}+HCO_3^-)$ versus $(Na^++K^+-Cl^-)$.

Table 2
The No. of samples exceeding allowable limits set by WHO.

Parameter	Polluted samples	
	A(2004)	B(2014)
TDS	770,1440	A299,A313,A441,B133,B158
TH	770,1911	A239,A275,A299,A313,A384, A411
Na		A409,B106,B138,B158
Ca	1645,1911	A178-B,A239,A275,A299,A313, A384,A441, B151,B167
Mg	770,1911	A239,A313,A327,A368,A384,A441,B167
F	405,770,1263	A225,A327,A368,A401,B106,B138
HCO_3^-	1375,827,480,481	A178-B, A208, A313,A327,A354, A386,A483,B133,B158,B167,B181
NO_3^-	24,720,721,729,1241,1287	A239,A275,A292,A299,A303,A308,A322,A323,A349,A354,A359,A372, A384,A390,A415,A422,A441,B104,B133,B151
SO_4^{2-}	1340,1364,1371,1420	A313,A352,A377,A409,B106,B133,B158

Table 3
Coordinate data of parameters from correspondence analysis.

Parameter	A(2004)		B(2014)	
	Factor loadings			
	F_1	F_2	F_1	F_2
TDS	0.0488	0.0160	0.0012	0.0567
TH	−0.0364	−0.0042	0.0274	−0.0627
Na			−0.0921	0.0874
Ca	−0.0371	0.0071	0.0270	−0.0333
Mg	0.0057	−0.0094	−0.0056	−0.0197
Mn			0.0022	−0.0016
F	−0.0029	−0.0003	−0.0066	0.0003
HCO_3^-	−0.1079	−0.0752	−0.0715	−0.1325
NO_3^-	−0.0550	0.1683	0.2853	0.0341
SO_4^{2-}	0.2184	0.0024	−0.0637	0.1354

research performed by Zhu et al. (2014) has shown that the region with high total hardness is consistent with nitrate pollution in the spatial distribution. Therefore, it is necessary to analyze the

relationship between total nitrogen (TN), TH and TDS (Fig. 6). The size of each bubble is a rough indication of the amount of the sampling points.

It can be observed in Fig. 6, TN and TH increased with time-being, and the mean value of group A is larger than that of group B. The TN and TH concentrations of agricultural area in 2014 are higher than the annual average, but the value of coal mining area is lower than the annual average value. One can draw a conclusion that the increased concentrations of TN relate to agricultural activities, being less affected by industrial production.

Nitrate is considered as inert and reactive and isotopic tracer, and its original concentration in nature can represent the predevelopment baseline (Edmunds and Shand, 2014). The potential for using NO_3^- as an indicator for contamination of ground water by sewage was discussed briefly by Marie and Vengosh (2001). The totalN (defined here as NO_3^- + TKN [TKN includes NH_4^+]) provided a reliable indicator. The decomposition of protein organic matter is associated with nitrate, ammonia nitrogen and nitrite formation. In nature, the presence of protein in groundwater is influenced by
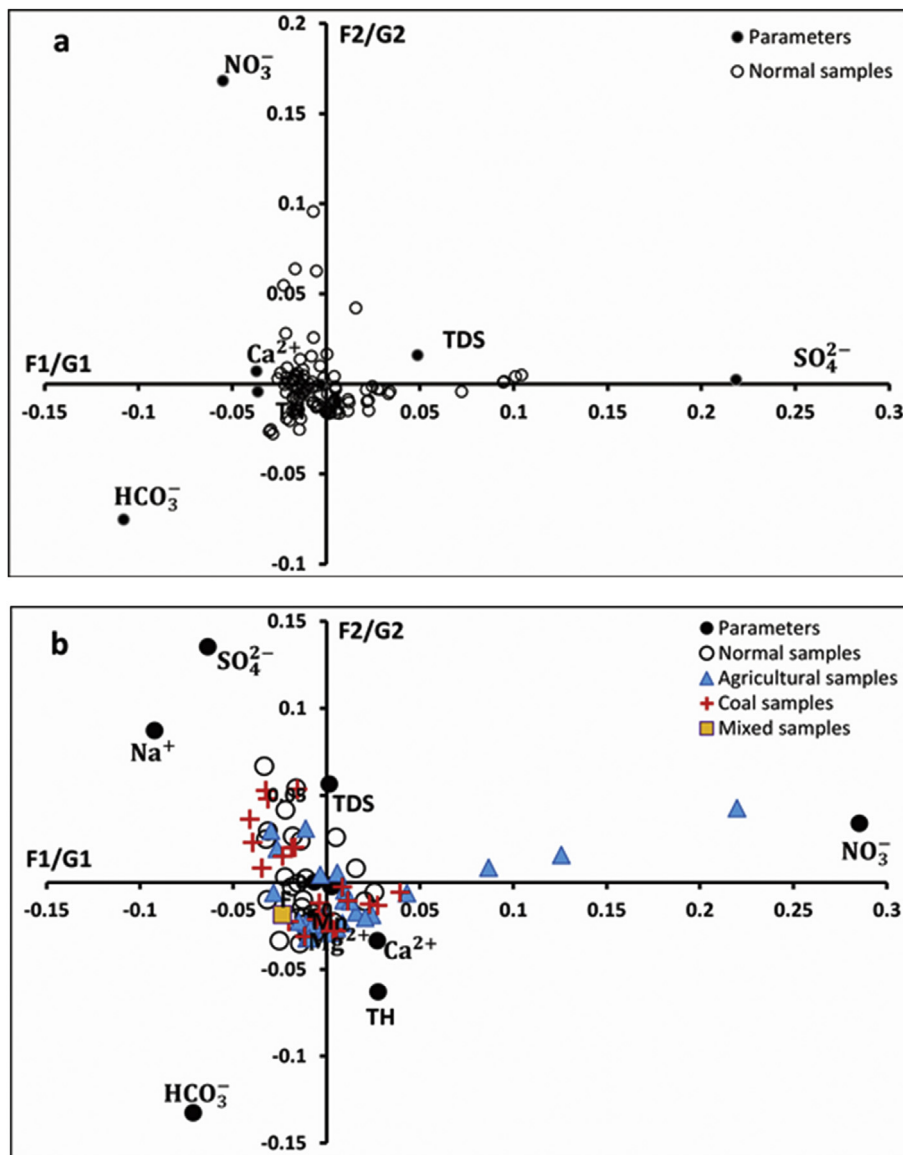
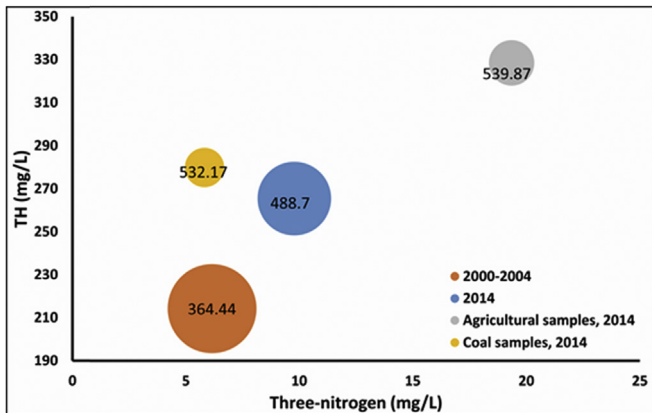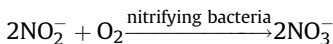**Fig. 5.** Correspondence analysis plane plots for data set A (upper) and B (lower).
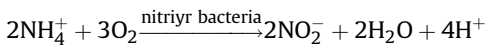
Fig. 6. The bubble chart of total nitrogen and TH (the number at the bubble indicates the value of TDS) .

anthropic activities, usually is the product of anthropogenic pollution. Mutual conversion may happen in the groundwater system under the certain conditions, nitrification is a key factor of affecting NO_3^- content of shallow groundwater, which is expressed as the following chemical reactions:

$$2NH_4^+ + 3O_2 \xrightarrow{\text{nitriyr bacteria}} 2NO_2^- + 2H_2O + 4H^+$$

$$2NO_2^- + O_2 \xrightarrow{\text{nitrifying bacteria}} 2NO_3^-$$

It can be seen in Table 1 that the concentrations of NH_4^+ and NO_2^- dropped by 0.23 mg/L and 0.04 mg/L, respectively, the concentrations of NO_3^- raised by 16.85 mg/L, was higher than the reduced value of NH_4^+ and NO_2^-. So there are other sources of nitrogen in addition to nitrification. Anthropic activities are the main factors resulting in nitrate pollution in northern Ordos Basin, and aquifer lithology is the auxiliary condition (Wang, 2006). The samples with higher NO_3^- concentrations mainly concentrated in region with intense anthropic activities and poor infrastructure. In agricultural area, a great deal of pesticide and fertilizer are used in the countryside, especially excessive use of nitrogen fertilizer, so amount of nitrogen is released into the soil, resulting in the rise of nitrate concentrations in groundwater. Pure industrial pollution has a minimal impact on the nitrate pollution (Zhu et al., 2014).

The higher concentrations of TH in groundwater can be explained from the following aspects: (i) Polluted and waste water, garbage, feces and other organic matter were converted into hydrogen nitrate and sulfuric acid during the oxidation and decomposition. The concentrations of Ca^{2+}, Mg^{2+} and TH will increase while calcium and magnesium minerals are exposed to dissolve by these acids; (ii) the discharge of mine pit water with low pH will result in the slat-effect by dissolving calcite and dolomite, which in turn will lead to the increase of TH; (iii) Excessive use of synthetic fertilizer will change acid-base environment in soil system, which may create the favorable conditions for dissolving calcium and magnesium salt.

4. Conclusions

Descriptive statistical method, Piper trilinear diagram, ratios of major ions and canonical correspondence analysis employed in this study help us to investigate the groundwater quality status in Salawusu aquifer system of Ordos Basin. Several conclusions obtained from the present study are summarized as follows:

(i) The contents of major ions in groundwater increased in 2014, but the average content of each parameter meets the permissible limit, so the overall groundwater quality in the study area is acceptable for drinking water. Higher values of TH and TDS in 2014 indicate the occurrence of the groundwater hardening.

(ii) The hydrochemical types of groundwater in the study area were more complex in 2014. In general, hydrochemical type mainly belongs to $HCO_3^- \cdot CO_3$-Ca·Mg facies with low salinity, and the hydrochemical types change from HCO_3^--CO_3^{2-} facies to SO_4^{2-}-Cl facies, and the type of $SO_4^{2-} \bullet$ Cl-Na increased during 10 years.

(iii) There are evaporation and concentration, lixiviation of rock salt, cation exchange and absorption in groundwater, explaining the reasons of the increasing concentrations of major ions in groundwater.

(iv) Groundwater hardness and nitrate pollution were identified in 2014, which was most likely caused by agricultural activities.

Acknowledgements

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