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ORIGINAL PAPER

Risk assessment of groundwater hydrochemistry for irrigation suitability in Ordos Basin, China

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Abstract
Irrigation water quality is of great concerns to the sustainable agriculture and often is neglected in most irrigation areas in Ordos Basin, a semi-arid area in China. In this paper, a hydrochemical investigation of groundwater was performed to highlight the groundwater quality and evaluate its risk/suitability for irrigation purpose in Ordos Basin. Hydrographical method, Piper diagram and PHREEQC geochemical modeling were employed to characterize the groundwater quality and the relevant geochemical processes. Electrical conductivity, sodium percentage (Na%), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), permeability index, magnesium ration (MR) and Kelley's ration (KR) were used to evaluate the suitability for irrigation purpose. In summary, 86.67% of the area is fresh water ($TDS < 1$ g/L) with HCO_3 type, brackish water (1 g/L $< TDS < 3$ g/L) with HCO_3, SO_4, $HCO_3 \cdot Cl$, $Cl \cdot SO_4$ type and salt water ($TDS > 1$ g/L) on the northwest side of the study area with Cl–Ca·Mg·Na type. The distribution of nitrate contents showed that nitrate pollution is a persistent problem that affects a wide area of the aquifer. The calculated Na%, SAR, RSC, MR and KR indicate that most of the groundwater is of acceptable risk for irrigation as well as for domestic usage. The Gibbs plot showed that the hydrochemistry of groundwater samples was mainly influenced by evaporation–precipitation and water rock dominance including carbonate and silicate minerals weathering.

Keywords Risk assessment · Groundwater pollution · Irrigation water · PHREEQC · Ordos Basin

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1 Introduction

The development of agriculture is a key factor in the socioeconomic growth of developing countries such as China. However, due to climate factor, rain-fed agriculture is becoming unreliable as a result of erratic rainfall and variable surface water flow in arid and semi-arid areas (Li et al. 2016). Therefore, groundwater exploitation has become a primary source for agricultural irrigation because it is reliable and readily available in relatively low cost. However, irrigated agriculture may exert negative impacts on river water quality due to the salt and agrochemical loadings brought by return flows. Irrigation water with poor quality will adversely impact the plant growth (Wanda et al. 2013). The adverse conditions will reduce agricultural production, which in turn, lowers agrarian economy thereby adversely affects the sustainable economic development (Rao 2006; Milovanovic 2007).

In recent years, groundwater pollution has become increasingly serious and has become a fairly common environmental problem throughout the world (Lambrakis 1998; Zhang 1998; Hosono et al. 2009; Purushotham et al. 2011; Rajesh et al. 2015; Li et al. 2016; Yang et al. 2016a, b). The increases in the amount of industrial wastewater, municipal solid wastes, domestic wastewater and frequent agricultural activities have led to the non-point source pollution, further aggravating groundwater pollution caused by the "3-Nitrogen" (ammonia, nitrite and nitrate); and significant increases in the total dissolved solids (TDS), total hardness, chlorides and sulfides in the groundwater in some regions caused serious reduction in available groundwater resources. At present, groundwater contamination risk assessment mainly consists of health risk assessment, groundwater vulnerability assessment, and risk assessment in light of specific vulnerability (Zhang et al. 2016). Little concerns have been paid on the risk of irrigated water. And the accurate understanding of hydrochemical characteristics and risk level is important to make better use of groundwater for irrigation purpose, especially in arid and semi-arid areas. Nevertheless, many groundwater supply plans in developing countries are implemented without paying enough attention to the risk concerns. Likewise, little concerns have been paid on irrigation water quality in Ordos Basin, and at present there is no established connection between the hydrogeochemical processes and irrigation water quality in Ordos Basin. It is therefore of great importance to establish the current status of groundwater quality and its risk level/suitability for irrigation purposes. The guidelines of water quality for agricultural use were promulgated by the Food and Agriculture Organization of the United Nations (FAO) (Ayers and Westcot 1985). The chemical compositions of irrigation water could pose impacts on the soils and crops, especially in the area with high saline alkali soil. Several indicators, salinity and sodium hazard, sodium absorption ratio (SAR), residual sodium carbonate (RSC), magnesium ration (MR) and Kelley's Ration (KR) can be used to evaluate the suitability of irrigation waters as a criterion (Bhuiyan et al. 2015; Li et al. 2016; Islam et al. 2017).

In this study, the groundwater hydrochemical risk assessment is carried out in the southeastern part of Ordos Basin, a Loess Plateau region, where substantial amount of groundwater has been exploited for irrigating farmland due to the dry climate. The objective of this study is to evaluate the risk level of groundwater hydrochemistry for the irrigation suitability. The results will provide useful insights for the present and future planning, protection and allocation of usable groundwater supplies for irrigation in Ordos Basin and elsewhere.

2 Study area

Ordos Basin, located at the northwest of China, belongs to the temperate continental monsoon climate zone in the eastern part of Eurasia, which is characterized with the scare precipitation and intensive evaporation, and the climate shows a typical seasonal change. According to the differences of climate features, Ordos Basin is divided into two climatic zones; the study area selected in this study belongs to the south temperate semi-arid zone, lies between North Latitudes 34°56′–37°7′ and East Longitudes 108°53′–110°37′ with a total area of about 22,127 km^2. The north of study area is primary watershed of Ordos Basin, the south boundary is the dividing line between Cambrian–Ordovician karst water system and Carboniferous and Jurassic fissure water, the west boundary is the dividing line between Cretaceous groundwater system and Carboniferous and Jurassic fissure water, and the east side of study area is the Yellow River.

The southeastern part of Ordos Basin is on the second ladder of the three major terrain steps in China. The study area belongs to the Loess Plateau area; the topography is relatively higher with altitudes between 1100 and 1700 m. The Yellow River and its tributaries are the primary surface water bodies. The mean annual temperature is about 3.6–13.6 °C. The average annual rainfall and evaporation is about 500 mm and 1500 mm, respectively.

2.1 Materials and methods

A total of 75 groundwater samples were collected in 500-mL polyethylene bottles from open dug wells during June to July 2015 from the Southeastern part of the Ordos Basin (Fig. 1). All these samples were analyzed with the standard methods of water chemical analysis. The accuracy of complete chemical analysis of a groundwater sample was measured by calculating the cation–anion charge balance, i.e., the total concentration of cations (TCC), and the total concentrations of anions (TCA). The ionic charge balance error should be within the limit of ± 5% (Li et al. 2016). In this paper, all samples balance error was below ± 5%, which is within the accepted limit and the correlation coefficient between TCC and TCA is 0.99.

3 Results and discussion

3.1 Data statistics

Mathematical statistical analysis can reflect the recent variations of the groundwater chemical composition. In this study, the pH, the total dissolved solids (TH), the total dissolved solids (TDS), the nitrate and the major ions were selected for hydrochemical analysis (Table 1).

In Table 1, the major chemistry of groundwater with the minimum, maximum, mean and standard deviation is summarized. The larger CV value indicates that ions are more sensitive to the external environment, such as the hydrological conditions, topography and anthropogenic activities. The concentration of Na^+, Ca^{2+}, Mg^{2+} and K^+ (meq/L) contributes to 36.34%, 34.35%, 28.77% and 0.54% of all the cations, respectively, and the abundance order is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. The order of anion abundance is $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$, contributing to 60.03%, 19.12%, 15.01%, and 5.84% to

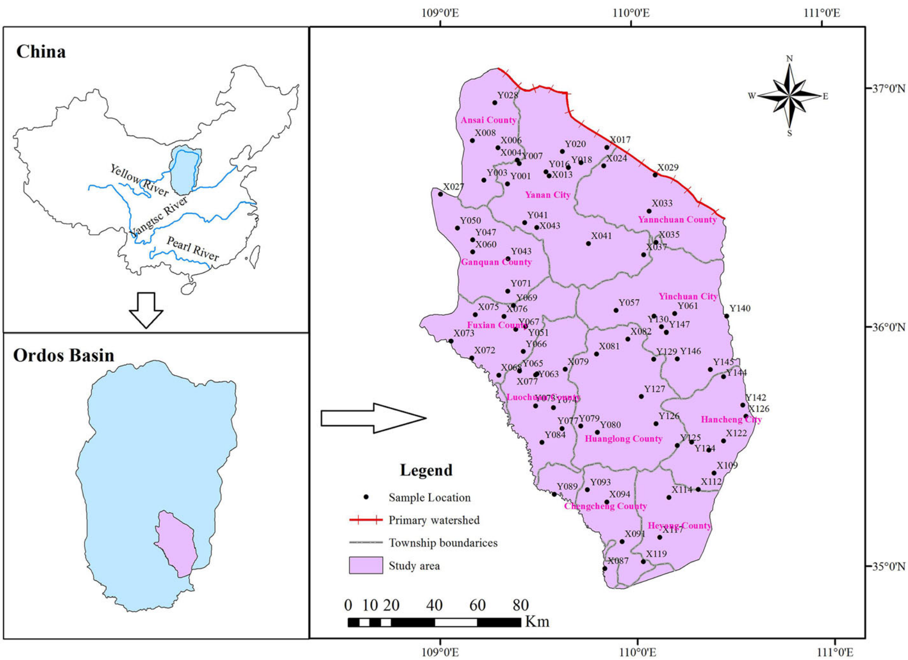

Fig. 1 Groundwater samples location of the study area

Table 1 Statistics of chemical parameters

Parameters	TDS (mg/L)	TH (mg/L)	pH	Na^{+} (meq/L)	Ca^{2+} (meq/L)	Mg^{2+} (meq/L)	K^{+} (meq/L)	HCO_3^{-} (meq/L)	SO_4^{2-} (meq/L)	Cl^{-} (meq/L)
Max	1994	1687	8.2	24.27	16.93	17.05	0.46	10.70	15.95	15.23
Min	219	86.08	7.17	0.32	0.53	0.94	0.01	2.82	0.05	0.07
Percentage (%)				36.34	34.35	28.77	0.54	60.03	19.12	15.01
Cv (%)	67.00	68.21	3.40	100.2	67.2	77.3	126.1	29.3	131.1	161.0

the total anions, respectively. The concentrations variation coefficient of K^{+}, Na^{+}, Cl^{-}, SO_4^{2-} and NO_3^{-} in study area is relatively large.

The pH value represents the ability of the water to react with the acidic or alkaline materials existing in the water. It can be seen from Table 1 that the pH value varies from 7.17 to 8.2 with a standard deviation of 3.4%, indicating a weakly alkaline environment. The suggested pH value for irrigation water is from 6.5 to 8.4 (Srinivasamoorthy et al. 2014). So the pH values of groundwater in the study area are within the acceptable limit of the irrigation water.

The value of total dissolved solids (TDS) ranged between 219 and 3488 mg/L, and standard deviation of 81.47%. According to WHO (2004) guidelines, the allowable limit of TDS is 1000 mg/L. Higher value (> 1000 mg/L) was detected in 13.3% of the samples.

High TDS are caused by an increase in dissolved components in the groundwater. It is possible that the groundwater in the study area is contaminated by nitrate, sulfate and so on, which makes the inorganic salt component in groundwater increase. Therefore, the total dissolved solids will increase correspondingly.

Hard water is measured with the calcium and magnesium content, generally expressed as the equivalent of calcium carbonate (Todd 1980). The total dissolved solids (TH) varied from 86.08 to 1687.16 mg/L. According to WHO international standard, the desirable limit of TH is 100 mg/L, and the allowable maximum limit of TH for drinking purpose is 500 mg/L, while Freeze and Cherry (1979) recommended that the most desirable limit is 80–100 mg/L. Groundwater with TH exceeding 500 mg/L is considered to be very hard one (Sawyer and McMcartly 1967). In the study area, 13% of groundwater samples exceed the maximum allowable limit of 500 mg/L.

Electrical conductivity is a good measure of salinity hazard to crops, so the higher electrical conductivity (EC) represents the groundwater environment with salt enrichment. For the classification purpose of irrigation water, the total concentration of soluble salts in irrigation water can be classified into three salinity zones: low ($EC \leq 250$ us/cm), medium (250–750 us/cm), high (750–2250 us/cm) and very high (2250–5000 us/cm). EC value ranged from 341.64 to 4360 us/cm. 40% of the samples are within the medium, and 53% of the samples fall in high salinity.

3.2 Hydrochemical facies

The change in hydrochemical types and total dissolved solids is controlled and influenced by topography, lithology, burial conditions and human activities. Under normal circumstances, with the change in TDS, the main ions in groundwater also change. Low TDS water, often with HCO_3^- and Ca^{2+} and Mg^{2+}; high TDS water with Na^+ and Cl^-; TDS medium groundwater, often dominated by SO_4^{2-}, major cations can make the Na^+, can also be Ca^{2+}. TDS are indicative parameters to reflect the groundwater quality in a region. Based on the level of TDS, groundwater type can be divided into fresh water ($TDS < 1$ g/L), brackish water (1 g/L $< TDS <$ 3 g/L) and saltwater ($TDS > 3$ g/L) (Zhang et al. 2011).

Hydrochemical facies is the combined effects of solution kinetics, rock–water interactions, hydrogeological settings and contamination sources, which can be used to describe groundwater differing in their chemical compositions. In this paper, Piper diagram (Piper 1944) was applied to perform the hydrochemical type's analysis. The hydrochemical types were found complex and diverse (Fig. 2). The whole of samples are mainly bicarbonate type water, and part distribution is mainly concentrated on bicarbonate sulfate type, bicarbonate chloride type, bicarbonate sulfuric chloride type and so on.

A TDS map was plotted by means of kriging and the fitted variogram technique (Fig. 3). It can be seen that 86.7% of the area is fresh water ($TDS < 1$ g/L). A small part of the region for brackish water (1 g/L $< TDS <$ 3 g/L), mainly distributing in the central area of Yan'an, the eastern of Ganquan County, the central part of Ansai county and south of the study area has a small distribution. Salt water ($TDS > 3$ g/L) only has a sample distribution in Ganquan County in the middle.

From the hydrochemical type of study area, for TDS less than 1 g/L of fresh water, in the anion triangle, the water samples on the left side of the triangle, poor chloride ions. In the cationic triangle, the water samples in the middle of the triangle and the sodium ion are relatively less. According to the distribution of the water samples in the diamond-shaped

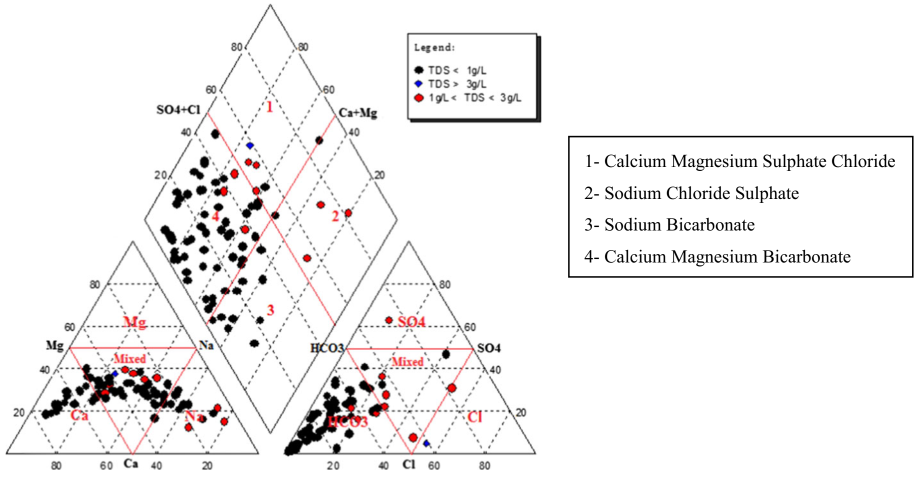

Fig. 2 Piper diagram of the groundwater samples in the study area

diagram, the hydrochemical types in the freshwater area are mainly HCO_3–Ca·Mg·Na (16), HCO_3–Ca·Mg (12), HCO_3–Na·Mg·Ca (10), HCO_3–Na·Mg (6), HCO_3–Na·Ca·Mg (7).

For 1 g/L < TDS < 3 g/L, in the anion triangles, most of the water samples fall in the middle of the triangle to the left. Moreover, compared with the water samples of TDS < 1 g/L, the anions shifted to the chloride ion direction, and the chloride ion content increased, and the individual water samples were located at one corner of the chloride ion. In the cation triangles, the water samples were inclined to the angle of sodium ion, and the content of calcium ion was decreased obviously. The type of water chemistry is based on HCO_3–Ca·Mg, HCO_3·SO_4–Mg·Ca·Na, with a small amount of water chemistry type SO_4–Na, HCO_3·Cl–Na·Mg·Ca, Cl·SO_4–Na.

For TDS > 3 g/L salt water in study area, there is only one sample. In the anion triangular diagram, the sample point is at the corner of the chloride ion, and the water chemistry type is Cl–Ca·Mg·Na. The TDS of Y047 was the highest, and the chloride ion was relatively high, which is located in Wangping Village beside the Luohe River. The water level was shallow and probably related to the use of pesticide.

3.3 Irrigation water quality

In irrigation area, groundwater extracted from the wells may contain substantial chemical components derived from the surrounding environment and human activities, which in turn may reduce crop yield and deteriorate soil fertility through lowing of osmotic pressure in the plant structural cells (Mohsen 2009). Understanding the quality of irrigation water not only helps the management changes for long-term productivity, but also has some guiding significance for increasing the yield of crops. Hence in this study, the risk level analysis of the groundwater for irrigation will be performed by evaluating the parameters such the NO_3^- (mg/L), sodium adsorption (SAR), percent sodium (Na%), residual sodium carbonate (RSC), permeability index (PI), Magnesium ration (MR) and Kelley's ratio (KR).

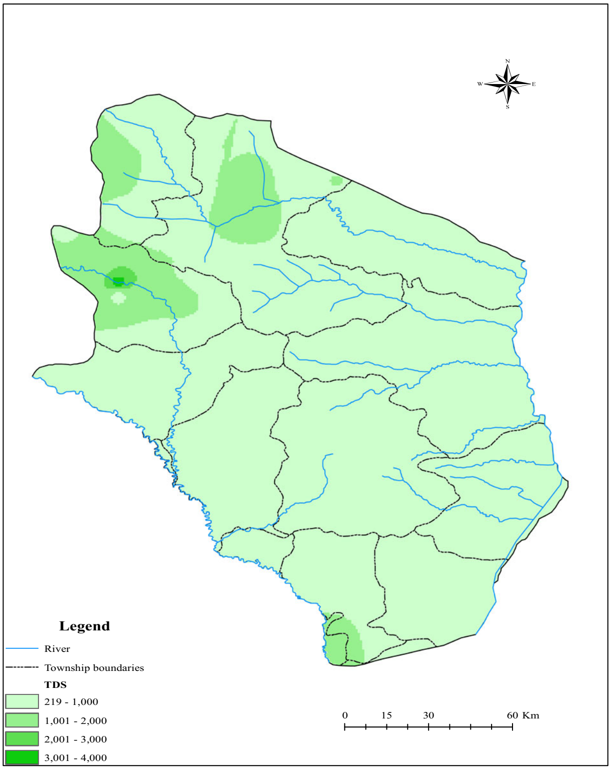

Fig. 3 The spatial distribution of TDS in the groundwater

3.3.1 Three nitrogen analysis in groundwater

Nitrate in groundwater refers to NO_3–N, NO_2–N and NH_4–N (nitrate nitrogen, nitrite nitrogen and ammonia nitrogen), where NO_3–N is a constant component and NO_2–N and NH_4–N are trace component. As we all know, NO_2–N has a greater harm to the human body, NO_3–N can also be reduced to NO_2–N in the human body, and NH_4–N in water can be converted to NO_2–N under certain favorable conditions (Cao 2012). Therefore, it is necessary to study the distribution of three nitrogen content.

The mean concentrations of NO_2–N, NH_4–N and NO_3–N in the study area are 0.046 mg/L, 0.028 mg/L and 38.65 mg/L. Therefore, the concentration of NO_3–N is only analyzed in this paper.

Forty-four water samples (58.7% of the total samples) exceed the WHO's drinking water standard, 10 mg/L for NO_3^- (WHO 2011). Long-term drinking of water with excessive amounts of nitrate may result in the health disorders, such as gastric cancer, goiter, birth hypertension and malformations (Cao 2012). The spatial distribution of nitrate concentrations was plotted using the fitted semivariogram model. In the right part of Fig. 7e, it can be seen that the high NO_3^- concentrations mainly occurred in the northwest of the study area. Moreover, the nitrate concentration tended to decrease gradually from northwest to southeast, and the maximum value appeared in the southwest of Yan'an City. Groundwater with NO_3^- concentration exceeding the limit of 3 mg/L NO_3^- is most probably contaminated by anthropogenic activities (Mohsen 2011). As much as 93% of the groundwater samples have NO_3^- concentration over the human affected value.

In the study area, the development of rivers has promoted the development of human activities such as intensive agricultural cultivation and raising livestock. The nitrogen most probably was derived from nitrogen fertilizer in agriculture region during the farming seasons. Regular application of N fertilizers is likely to create a permanent source of NO_3^- especially in irrigated area. Nitrogen that was not absorbed by plants would get into the water by leaching, thereby increasing groundwater NO_3^- concentration. During the downward migration of NO_3^-, flood irrigation and large rain events played a catalytic role (Mohsen 2011). Additionally, in urban groundwater of study area, the main sources of nitrate were mainly related to domestic sewage and solid waste disposal.

3.3.2 Sodium adsorption ratio (SAR)

In the farmland irrigation area, irrigation water quality and alkalinity need to be analyzed in order to make a reasonable assessment of irrigation water (Rhoades 1972). SAR is a very important measure of the alkali or sodium hazard to crops. The smaller the SAR, the better it is for the growth of plants, because the sodium ions with high concentration are prone to be adsorbed onto the clay particles, displacing Mg^{2+} and Ca^{2+} ions. Exchange of Na^+ for Ca^{2+} and Mg^{2+} results in a soil with a poor internal channel and impose the restrictions on the circulation of water and air in wet conditions (Rao 2006). Such soil usually form unmanageable and hard colds in dry conditions and is bad for crops. The following formula is adopted in SAR calculation (Alrajhi et al. 2015):

$$\mathrm{SAR} = \frac{\mathrm{Na}^+}{\sqrt{\frac{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}}{2}}}$$

where the concentration is presented in meq/L. The analytical data were plotted (Fig. 4) on the US salinity diagram (USSL 1954). This chart consists of EC for abscissa and SAR for ordinate. The two axes are divided into four major zones, i.e., S_1–S_4 represents the salinity zone from low to very high, and C_1–C_4 from low to very high EC, respectively. The SAR values in the area vary from 0.22 to 13.5 meq/L (Fig. 7a). It is obvious that water classes of groundwater samples are C_2–S_1 (40%), C_3–S_1 (52%), C_4–S_1 (1%), C_3–S_2 (1%), C_4–S_2 (1%) and C_5–S_1 (1%). In the C_2–S_1 (medium-salinity hazard and low-sodium hazard) and C_3–S_1 (medium–high-salinity hazard and low-sodium hazard) classification, the proportion is higher, and they can be applied to all types of soil with little danger for exchangeable sodium for irrigating (Gedamy et al. 2017). Four percent of the groundwater samples fall in the zone of C_4–S_1 category indicating a water of high-salinity hazard and medium-sodium hazard, which can be suitable for plants having good salt tolerance but unsuitable for irrigating the soil with restricted drainage conditions. As a result, most of the water from this aquifer is generally suitable for irrigation.

3.3.3 Sodium percentage (Na^+%)

The concentration of sodium in the soil also plays an important role. Most salts of Na are not active in chemical reactions even though they are prone to be solved in water (Pradhan and priasteh 2011). The high sodium concentration can make the soil harden and reduce the permeability of the soil (Islam et al. 2017). In addition, excessive salinity can exert harmful impacts on plant growth physically by limiting the absorption of water and

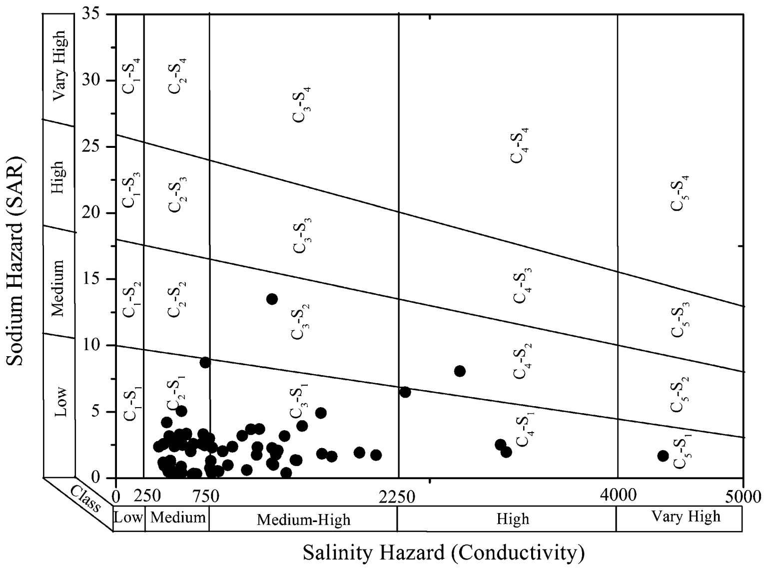

Fig. 4 Salinity and alkalinity hazard of irrigation water in US salinity diagram

nutrients through modifying the osmotic processes and chemically by metabolic reactions (Rao et al. 2012). The sodium percentage (%Na^+) is calculated using the expression below:

$$\%\mathrm{Na} = \left(\frac{\mathrm{Na}^+ + \mathrm{K}^+}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^+ + \mathrm{K}^+}\right) \times 100$$

where all ionic concentrations are in meq/L. Wilcox (1995) uses sodium percent (%Na) and EC indicators to classify irrigation water quality. Figure 5 shows all the samples on the Wilcox diagram, and the calculated values are summarized in Table 2. It can be seen in Fig. 5 that water samples were in the fields of good-permissible, doubtful-unsuitable, unsuitable, permissible-doubtful and excellent-good, accounting for 35%, 3%, 4%, 4% and 54% of the total groundwater samples, respectively. The spatial variation shows the Na% of the study area decreases from middle to the north and north in two directions (Fig. 7b).

3.3.4 Residual sodium carbonate (RSC)

High concentrations of carbonate ions (CO_3^{2-} + HCO_3^-) tend to precipitate with alkaline soils (Ca^{2+} + Mg^{2+}) through chemical reaction, increasing the percent content of Na^+, thereby affecting water quality. When carbonate ions is larger than alkaline earths, the excess carbonate ions will form $NaHCO_3$ by combining with Na^+, thus affecting the sudden structure, which is called RSC (Eaton 1950). And, the meaning of RSC is the difference between carbonate ions minus alkaline earths, which is expressed as (Vasanthavigar et al. 2012):

$$\mathrm{RSC} = \left(\mathrm{CO_3}^{2-} + \mathrm{HCO}_3^-\right) - \left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right)$$

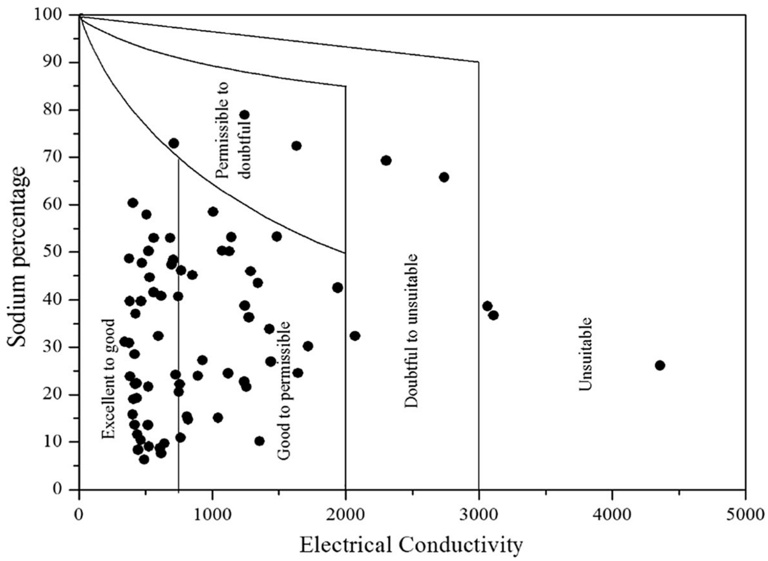

Fig. 5 Sodium percentage and EC of groundwater classification for irrigation uses

Table 2 Suitability of groundwater for irrigation based on irrigation water index

Parameters	Range	Class	Number of samples	Percentage of samples
NO_3^-	≤ 2	Excellent	3	4
	2–5	Good	5	6.7
	5–20	Permissible	43	57.3
	20–30	Doubtful	4	5.3
	> 30	Unsuitable	20	26.7
SAR	< 10	Excellent	74	98.7
	10–18	Good	1	1.3
	18–26	Doubtful	0	0
	> 26	Unsuitable	0	0
Na%	< 20	Excellent	18	24.
	20–40	Good	29	38.7
	40–60	Permissible	22	29.3
	60–80	Doubtful	6	8
	> 80	Unsuitable	0	0
RSC	< 1.25	Safe	54	72
	1.25–2.5	Doubtful	11	14.7
	> 2.5	Unsuitable	10	13.3
MR	< 50	Suitable	71	94.7
	> 50	Unsuitable	4	5.3
KR	< 1	Suitable	61	81.3
	> 1	Unsuitable	14	18.7

where the concentrations are presented in meq/L. RSC ranges from − 30.82 to 6.33 meq/L with an average of − 0.6 meq/L. The classification of groundwater according to RSC values is summarized in Table 2, where 72%, 14.7% and 13.3% of the sampling points fall into the categories of good, doubtful and unsuitable, respectively for irrigation purpose. High RSC (> 2.5) means increase the adsorption of Na^+ in soil, decreased the permeability of the soil, and unsuitable for plant growth. The interpolated image (Fig. 7c) reveals good, doubtful category and high RSC (> 2.5) samples are scattered.

3.3.5 Permeability index (PI)

PI indicates the suitability rate of water for irrigation, which is classified by Doeen (1964). The permeability of soil is greatly affected by the concentration of sodium, calcium, magnesium and bicarbonate chemical components in soil, and it also affects the quality of irrigation water in long-term utilization (Davraz and Özdemir 2014). According to the PI, the groundwater can be classified into three classes: class I, class II and class III. Class I is the maximum permeability of 100% that is suitable for irrigation. Class II, which is 75% maximum permeability, is marginally suitable for irrigation. The class III, which shows 25% maximum permeability, is not suitable for irrigation. PI is calculated as follows:

$$\mathrm{PI} = \frac{\mathrm{Na}^+ + \sqrt{\mathrm{HCO}_3^-}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}} \times 100$$

All ions concentrations are expressed in meq/L. The analytical data plotted on the charts (Fig. 6). PI ranging from 28.2 to 99.0 with average of 62.8. According to PI values, approximately 73% of the groundwater samples fall in class I, which indicates the water is moderate to good for irrigation purpose. 21% of groundwater samples lie under the class II

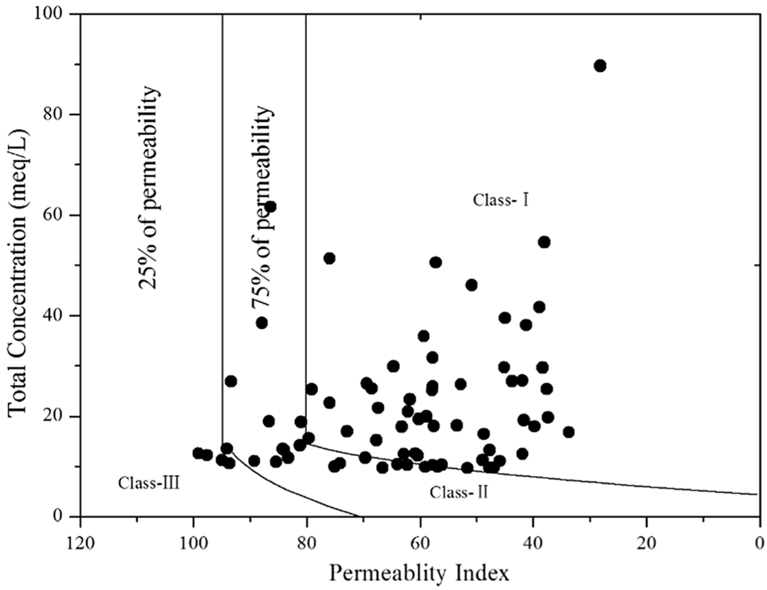

Fig. 6 Suitability of groundwater for irrigation based on PI

(marginally suitable) and the rest of the groundwater are under the class III (unsuitable for irrigation).

3.3.6 Magnesium ratio (MR)

Magnesium ratio used for assessing the water suitability for irrigation was proposed by Szabolcs and Darab (1964) and redefined by Raghunath later (1987). In most groundwater, the calcium and magnesium ions keep in equilibrium state (Hem 1985), and usually they do not show equal behavior in the soil system. Normally, a high level of Mg^{2+} is caused by exchanging with Na^{+} in the irrigated soils, which may cause soil assemblages to disperse and damages soil structure particularly when water contains more Na^{+} and high saline (Rao et al. 2012). The extent of the effect of magnesium ions on irrigation water is indicated by MR. In Mg^{2+}-dominated water (MR > 50), it is considered harmful and unsuitable for irrigation purposes because it has adverse effects on the crop yields. MR is calculated as:

$$MR = \left(\frac{Mg^{2+}}{Mg^{2+} + Ca^{2+}}\right) \times 100\%$$

In which, the ionic concentrations unit is meq/L. In study area, the MR values range from 13.13 to 71.72. Results show that approximately 5.3% of samples exceeds the value of 50, which are not suitable for irrigation. The high MR (> 50) of study area mainly distribution in the northern part of Yan'an City and the southern of Chengcheng County (Fig. 7d). If continuous use of water with high concentrations of magnesium will adversely affect soil quality and crop yield. In the remaining water samples, the MR is less than 50 and hence they are suitable for irrigation.

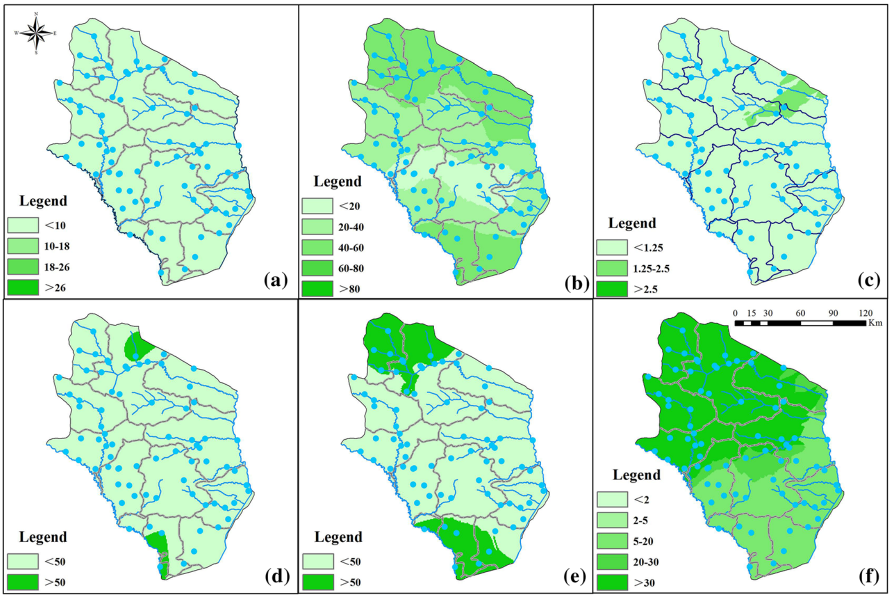

Fig. 7 **a** Distribution of SAR; **b** distribution of Na%; **c** distribution of RSC; **d** distribution of MH; **e** distribution of KR; **f** distribution of NO_3^-

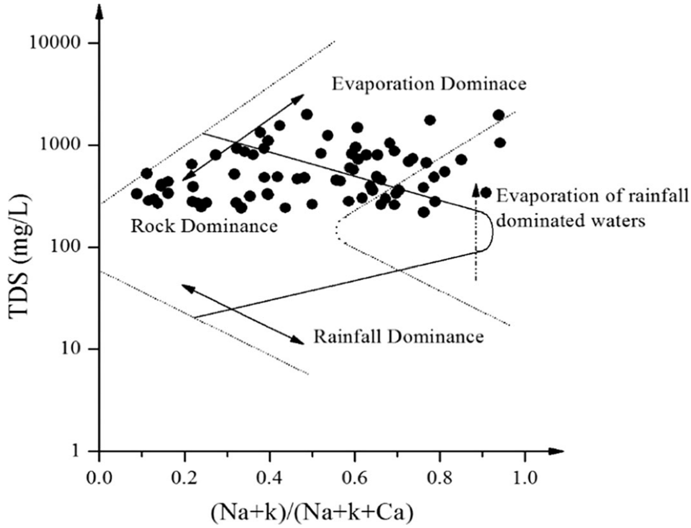

Fig. 8 The weight ratio of $(Na^+ + K^+)/(Na^+ + K^+ + Ca^{2+})$

3.3.7 Kelley's ration (KR)

Kelley ration is put forward by Kelley (1940) and Paliwal (1967), which is an important index for the classification of water for irrigation purposes. Degree of irrigation quality can be classified as suitable, if the KR less than 1; Unsuitable, if the KR is more than 1 (Islam et al. 2017). The formulation of KR is:

$$KR = \frac{Na^+}{Ca^{2+} + Mg^{2+}}$$

where ions concentrations are denoted in meq/L. The value of KR ranges from 0.06 to 3.74 with an average of 0.66 (Fig. 7e). The classification of KR demonstrates that approximately 81.3% of samples are suitable for irrigation (Table 2).

3.3.8 Evaporation and precipitation

Gibbs (1970) recommended a diagram to illustrate the mechanisms dominating the water chemistry. Based on the Gibbs diagram, there are three majors mechanisms: (1) rock dominance (2) evaporation dominance and (3) rainfall dominance (Fig. 8; Zhao et al. 2016; Liu et al. 2015). Gibbs diagram is composed of horizontal and vertical coordinates, in which the abscissa is ratio of $(Na^+ + K^+)$ to $(Na^+ + K^+ + Ca^{2+})$, and the ordinate is TDS.

It can be seen that the density of distribution of all samples mainly falls in the evaporation dominant and rock dominant category, suggesting chemical weathering and evaporation–precipitation are the predominant processes controlling the groundwater hydrochemistry in the study area (Fig. 8). Evaporation is capable of removing moisture while salt remains in water. As time goes on, the groundwater solution is gradually enriched, and the TDS increases continuously. Thus, the salts with less solubility are saturated in water and precipitated successively. The ions of soluble salts gradually become

Table 3 Saturation indexes of minerals in groundwater using PHREEQC

	Calcite	Dolomite	Fluorite	Gypsum	Halite
Max	1.24	1.85	− 0.51	− 0.8	− 5.11
Min	− 0.15	− 0.06	− 2.19	− 3.38	− 8.96
Mean	0.53	1.08	− 1.70	− 2.06	− 7.44

the main components, mainly distributed in the shallow drainage area, which is near the Yellow River and its tributaries. The rock–water interaction represents the interactions between the constitutes of rock and the groundwater, which makes it possible to transfer part of the material into the ground water, mainly in the deep underground water (Cao 2012; Yang et al. 2016a, b). The Gibbs diagrams can explain the natural factors controlling the groundwater chemistry, but the influence of human activities cannot be ignored.

3.3.9 Mineral saturation index

The groundwater and the aquifer medium together constitute a geochemical system containing both solid and liquid phases. If the liquid and solid phases in the system are in an unbalanced state, dissolution or precipitation occurs. The mineral equilibrium calculation can be predicted the thermodynamic control on the composition of the groundwater that has equilibrated with various minerals. The saturation index method is the most widely used method in the judgement and research of mineral relative groundwater saturation. "Saturation index" can be used to determine the water rock gas in the hydrogeochemical system, under the action of the crustal thermodynamics of chemical elements continue to occur in the phase transformation and change laws. The SI was calculated by PHREEQC models for all groundwater samples, which is defined in Equation as (Li et al. 2010):

$$\mathrm{SI} = \mathrm{Lg}\frac{\mathrm{IAP}}{K_{\mathrm{SP}}}$$

where IAP is the ion activity product; K_{SP} is the equilibrium constant. If the mineral and groundwater are kept in an equilibrium state, the SI should be close to 0, the range of which is generally considered as 0 ± 0.5 (Li et al. 2016). It mains that the tendency of mineral neither to dissolve into, nor precipitate from groundwater. If the SI more than 0, minerals are supersaturated in comparison with groundwater and vice versa.

The calculated values (Table 3) of SI for halite, dolomite, calcite, fluorite and gypsum range from − 8.96 to − 5.11, − 0.06 to 1.85, − 0.15 to 1.24, − 0.51 to − 2.19 and − 3.38 to − 0.8 with mean of − 7.44, 1.08, 0.53, − 1.7 and − 2.06 respectively. In about 96% of groundwater samples of calcite and dolomite was more than 0, indicating oversaturation with respect to those minerals due to evaporation, and they are precipitated. Halite was obviously under saturated and tends to dissolve into the groundwater. All of the samples were below or in an equilibrium state with gypsum and fluorite.

4 Conclusions

The integration of statistical and geochemical approaches was applied to explore the hydrochemistry of groundwater and its risk level/suitability for irrigation utilization at the southeastern part of Ordos Basin. It was found that the geochemistry of groundwater displays $Na^+ > Ca^{2+} > Mg^{2+} > K^+$, $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$ trend, and 86.67% of the area is fresh water (TDS < 1 g/L) with HCO_3 type, and changing to brackish water (1 g/L < TDS < 3 g/L) with HCO_3 type, SO_4, $HCO_3{\cdot}Cl$, $Cl{\cdot}SO_4$ along the groundwater flow direction (near the Luohe River upstream), and salt water (TDS > 1 g/L) on the northwest side of the study area. It is mainly due to the impact of human activities.

TH, pH, TDS and other major ions are within the specified limits for drinking and irrigation purposes. The high NO_3^- in the groundwater may be caused by over application of manures as fertilizer, wastewater and solid waste disposal. Several parameters, SAR, RSC, Na%, PI, MR and KR, have been calculated to evaluate the groundwater suitability for irrigation use. The results demonstrate that 91% of the groundwater is free of risk for irrigation purpose. The Na% value of majority of the samples suggests their suitability for irrigation. The RSC values indicate most groundwater samples are suitability for irrigation with few exceptions in certain locations. The PI suggests groundwater quality is moderate to good for irrigation.

The Gibbs plot indicates that the hydrochemistry was predominantly controlled by chemical weathering and evaporation–precipitation. Water–rock interaction, mainly includes dissolution of carbonate mineral and silicate weathering. The PHREEQC models suggested that in about 96% of groundwater samples of calcite and dolomite was oversaturation. Obviously, halite in groundwater did not reach saturated; the trend has continued to dissolve.

Knowledge on irrigation water quality can help farmers to choose some alternatives faced to the potential water quality problems that might reduce crop production. The results will provide useful insights for the present and future planning, protection and allocation of usable groundwater supplies for irrigation in Ordos Basin and other similar areas worldwide.

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