

Evaluation of groundwater quality and health risks from contamination in the north edge of the Loess Plateau, Yulin City, Northwest China

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Abstract Groundwater is a vital source for domestic and irrigation purposes in the loess area of Northwest China where climate is arid. However, the quality of groundwater in this area is deteriorating due to intensive industrial and agricultural activities, and this has a great adverse impact on human health. In order to better understand the pollution status of groundwater and the health risks to local residents, comprehensive water quality index was applied to assess the quality of drinking water in Yulin City, Northwest China, and sodium adsorption ratio, sodium percentage, residual sodium carbonate and permeability index were used to evaluate the quality of irrigation water. Moreover, the health risks caused by ingestion of groundwater were evaluated using the model proposed by the Ministry of Environmental Protection of the PR China. The results show that all groundwater samples for irrigation will not induce soil salinization, but more than half of them are not suitable for drinking, and Fe, Mn, TH, Mg²⁺ and NO₃-N are the common contaminants which are mainly from natural processes, industrial and agricultural activities. The health risk assessment indicates that children face greater non-carcinogenic risk than adults. The order of contribution of contaminants to non-carcinogenic risk is

NO₃⁻ > As > F⁻ > Fe > Mn > Ba²⁺ > Cr⁶⁺ > Zn > NO₂⁻. The average carcinogenic risk of carcinogens (Cr⁶⁺ and As) is 1.17×10^{-4} and 1.37×10^{-4} for adults and children, respectively, which surpasses the permissible level (1×10^{-6}) stipulated by the Ministry of Environmental Protection of the PR China. Hence, effective measures are highly demanded to manage groundwater pollution and reduce the risks to human health.

Keywords Groundwater chemistry · Water quality assessment · Health risk assessment · Loess area · Yulin City

Introduction

As an important part of water resource as well as the major source of agricultural, industrial and domestic water, groundwater plays a significant role in securing resident life, supporting socioeconomic development and maintaining ecological balance (Su et al. 2014a, b). It is estimated that groundwater consumption in the world accounted for about 50, 40 and 20% of the amount of domestic water, industrial water and irrigation water, respectively (Tai et al. 2012). In China, groundwater is used as the main drinking water source in about two-thirds of the city (Zhang et al. 2009). Especially in the arid and semiarid area, groundwater is often the only source of drinking water supply (Li 2016). In recent years, with the expansion of urban scale, the growth of population and the rapid development of economy, domestic and industrial wastewater is discharged, a variety of garbage is piled up at random, and pesticides and fertilizers are excessively used, posing a significant adverse effect on groundwater quality

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(Li et al. 2012, 2016a; Qian et al. 2012; Wu et al. 2014a). The most common contaminants in groundwater include arsenic (Alam et al. 2015), fluorine (Li et al. 2014a), nitrogen (Suthar et al. 2009) and organic contaminants (Hu et al. 2016). In particular, the large-scale land-creation projects in the loess regions of Northwest China have changed the vulnerable groundwater environment (Li et al. 2014b), and the creation of the “Silk Road economic belt” between China and Central Asia in 2013 may cause deterioration of groundwater quality (Li et al. 2017a, b). Therefore, it is essential to carry out groundwater quality research, especially in these areas where groundwater quality is influenced significantly by human activities (Li 2016; Li et al. 2017b).

In recent decades, a number of scholars have conducted in-depth researches on the dynamics of groundwater pollution and have attained significant results (Wen et al. 2013; Li et al. 2016b; Rasool et al. 2016). Chidambaram et al. (2014) investigated the metal contamination of groundwater in an industrial concentration district of Tamil Nadu, finding that the major metals that cause the deterioration of groundwater quality are Cr^{6+} , Mn, Zn, Fe, As, Cu, Cd and Pb, and these toxic pollutants are mainly from local industrial activities. Hudak (2010) carried out a detailed study on the potential sources of groundwater contamination in a portion of the Trinity Aquifer of USA and found that the contaminants are mainly derived from agriculture and oil production. Their study provides guidance for other groundwater researchers to investigate the local groundwater quality. Li et al. (2016b) assessed groundwater quality and provided some measures for the protection and management of groundwater in Hua County, China. Their detailed study shows that human interference is the main cause of deterioration of groundwater quality, and their recommendations may be useful for local groundwater managers to manage contaminated groundwater.

Recent years, many scholars have used a variety of methods for their respective research areas of the groundwater quality evaluation (Li et al. 2010; Wu et al. 2011, 2014b). Fagbote et al. (2013) applied entropy-weighted method to evaluate the groundwater quality in the farm settlements in Western Nigeria. The same method was also adopted by Li et al. (2014c) to assess groundwater quality in an industrial park in China. Mohebbi et al. (2013) described the overall situation of groundwater quality in urban areas of Iran using an improved water quality assessment method based on the Canadian water quality index. Yidana et al. (2010) evaluated the groundwater quality in Hashtgerd plain by means of multivariate statistical techniques. These statistical techniques include factor analysis, cluster analysis, discriminant analysis and principal component analysis. Li et al. (2016c) carried out an

assessment of groundwater quality and health risks caused by the contaminants in a traditional agricultural region of Northwest China. Similarly, the health risk assessment of hazardous substances in groundwater was carried out by Batayneh (2012), Chen et al. (2016) and Ryu et al. (2007) independently to quantify the impact of different hazardous substances on human health. These studies indicated that the main way to pose carcinogenic and non-carcinogenic risks was to ingest contaminated groundwater. Al-Rawabdeh et al. (2014) utilized an integrated model to evaluate the quality of contaminated groundwater in Houston County, Minnesota. This integrated model is a combination of Geographic Information Systems (GIS) and DRASTIC model recommended by the United States Environmental Protection Agency (USEPA). Dahiya et al. (2007) proposed an approach based on fuzzy sets theory to eliminate the adverse effects of uncertainty factors on groundwater quality evaluation in imprecise environment. In addition, electrical resistivity tomography (Rao et al. 2013), neural network (Sirat 2013), set pair analysis (Li et al. 2011) and matter element extension analysis (Li et al. 2016c) have been widely used in the identification of groundwater pollutants and the evaluation of groundwater quality. Hence, it is confirmed that these methods are more trustworthy for groundwater quality assessment.

Groundwater is exploited in the loess area of Northwest China for various purposes such as domestic, agriculture and industry uses (Qian et al. 2013). Yulin City is located in the north edge of the Loess Plateau of China. Loess is a homogeneously porous media. The pores among the loess are quite small, which makes the loess formation difficult to yield large quantity of groundwater, which make groundwater much more precious in the loess area. In Yulin City, groundwater is heavily used for drinking and irrigation by local residents due to the lack of fresh surface water, which burdens the pressure of groundwater quantity in this area. Particularly, groundwater quality is deteriorating at an alarming rate due to intensive human activities. According to the statistical data of 2010, the discharge of wastewater and waste residue in this area was 4798.75×10^4 t and 1462.36×10^4 t, respectively (Zhu 2012). The random discharge of these pollutants has resulted in the deterioration of the local groundwater quality. Drinking contaminated groundwater can cause great health risks to local residents. However, the extent of groundwater pollution and associated health risks has not been reported. Therefore, the purposes of this research are (1) to analyze groundwater hydrogeochemical characteristics and formation mechanisms; (2) to evaluate the groundwater quality for drinking and irrigation purposes; and (3) to assess the health risks caused by drinking water intake pathway to adults and children. This study will provide substantial scientific information which helps to

improve the groundwater quality management and protection for human health.

Study area

The study area is situated in the northern part of Shaanxi Province within latitude 38°05'34.2"–39°19'43.1"N and longitude 109°34'10.2"–109°55'13.1"E. This area belongs to the transition zone of the Loess Plateau and Mu Us desert. It is bounded by Shenmu County in the north, Hengshan County in the south, Wushen County in the west, and Jia County and Mizhi County in the east, covering about 1,300 km² (Fig. 1). The area belongs to the arid and semiarid continental climate zone. According to the observational data of Yulin meteorological station from 1978 to 2010, the annual average temperature is 8.1 °C. The average annual precipitation is 368.9 mm, 63% of which concentrated in July, August and

September. The average annual evaporation is 1195.5 mm, which is 2.89 times higher than the annual precipitation. The Yuxi River which runs through the middle of the study area from north to south is the biggest river in the study area (Fig. 1). The average annual runoff is $3.711 \times 10^8 \text{ m}^3$. It has nine tributaries from north to south: Baihe River, Qiqiu River, Wudao River, Erdao River, Toudao River, Qinhe River, Shahe River, Qingyun River and Liuqian River. Because of industrial and domestic wastewater discharge, almost all of the rivers are severely polluted and thus cannot be used for drinking and irrigation.

The aquifer in the study area is classified into the loose rock pore aquifer, loose rock fracture aquifer and clastic rock fracture aquifer. This study focuses on the loose rock pore aquifer which is mainly composed of the Quaternary aeolian sands, alluvial sands and gravels. The thickness of this aquifer ranges from 10 to 70 m, and the yield of a single well ranges from 47.58 to 1824 m³/d. The

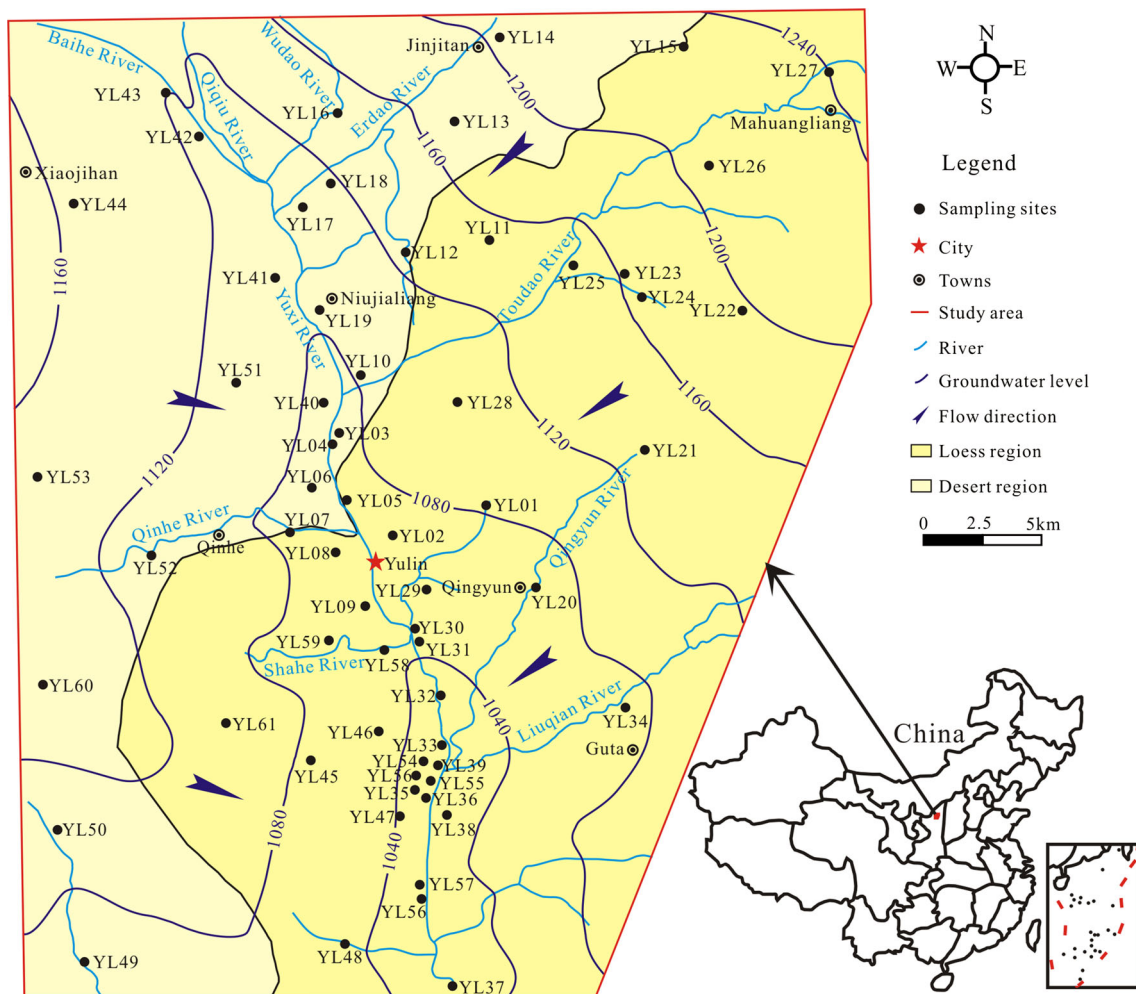


Fig. 1 Location of the study area and groundwater sampling points

groundwater in the study area receives recharge from many sources including precipitation infiltration, lateral flow and irrigation infiltration. Groundwater runoff is dominated by topography, geomorphology and the geological structure of the aquifer. The flow direction of groundwater in the study area is generally from both east and west to the Yuxi River (Fig. 1). Evaporation, springs and artificial abstraction constitute the major components of groundwater discharge.

Materials and methods

Sample collection and analysis

For this study, sixty-one groups of groundwater samples were collected from monitoring wells during September 2011. Before sample collection, every well was pumped for a few minutes to ensure the elimination of the adverse effects of stagnant water. And then groundwater samples were collected using 1.5-L polyethylene bottles which were thoroughly washed three times using the well water before sampling. Besides, pH and electrical conductivity (EC) of groundwater were measured by the German-made multifunctional portable tester (Multi-340i/SET) at each sampling site. All of the sampling sites, as shown in Fig. 1, were accurately recorded by a handheld GPS. All the collected samples were transported immediately to the Groundwater Mineral Water and Environmental Monitoring Centre of Ministry of Land and Resources in China for physiochemical analysis. The collection, preservation, transportation and measurement of groundwater samples were carried out in accordance with the standard methods prescribed by APHA (2012).

Each groundwater sample was tested for major ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and HCO_3^-), nitrate (NO_3-N), nitrite (NO_2-N), fluoride (F^-), silicate ($H_2SiO_3^-$), total hardness (TH), total dissolved solids (TDS), chemical oxygen demand (COD_{Mn}) and heavy metals (Fe, Mn, Zn, Ba^{2+} , Cr^{6+} and As). K^+ and Na^+ were measured using flame atomic absorption spectrophotometry; Ca^{2+} , Mg^{2+} and TH were analyzed using ethylene diamine tetraacetic acid (EDTA) titration; Cl^- , HCO_3^- and Ba^{2+} were determined using titration; SO_4^{2-} and F^- were tested by ion chromatography; NO_3-N was analyzed by phenol disulfonic acid spectrophotometry; NO_2-N was determined by spectrophotometry; $H_2SiO_3^-$ was determined by silicon molybdenum blue spectrophotometry; TDS was tested using drying and weighing; COD_{Mn} was determined by dichromate method; Fe, Mn, Zn and Cr^{6+} were determined by means of inductively coupled plasma atomic emission spectrometry; and As was measured by atomic fluorescence spectrometry. In the process of analysis of the hydrogeochemical parameters of groundwater, duplicates were completed to ensure the reliability of the analysis results.

Groundwater quality evaluation

Drinking water quality evaluation

According to the comprehensive water quality index (CWQI) stipulated by the Quality Standard for Groundwater of China, groundwater quality can be classified into five ranks: rank I (excellent), rank II (good), rank III (medium), rank IV (poor) and rank V (extremely poor) (Bureau of Quality and Technical Supervision of China 1993; Li et al. 2014d). Based on the standard, the specific calculation steps of CWQI are as follows:

$$(F_i)_{\text{mean}} = \frac{1}{n} \sum_{i=1}^n F_i, \quad (i = 1, 2, \dots, n) \quad (1)$$

$$F = \sqrt{\frac{(F_i)_{\text{mean}}^2 + (F_i)_{\text{max}}^2}{2}}, \quad (i = 1, 2, \dots, n) \quad (2)$$

where F_i denotes the evaluation value of each parameter; $(F_i)_{\text{mean}}$ and $(F_i)_{\text{max}}$ represent the mean and maximum values of F_i , respectively; n represents the number of parameters selected for water quality assessment. The classification of groundwater quality based on CWQI is shown in Table 1.

Irrigation water quality evaluation

Groundwater irrigation is the main cause of soil salinization–alkalization in arid and semiarid areas (Li et al. 2013a, b). In the study area, groundwater is the only source of irrigation water. Therefore, irrigation water quality evaluation was necessary in order to inform the local agricultural managers of the degree of soil salinization–alkalization posed by groundwater irrigation. Sodium adsorption ratio (SAR) is an important index to measure the soil alkali hazard caused by irrigation water (Xiao et al. 2016; Wu et al. 2017). The SAR is calculated by formula (3):

$$SAR = \frac{Na^+}{\sqrt{\frac{Mg^{2+} + Ca^{2+}}{2}}} \quad (3)$$

where Na^+ , Mg^{2+} and Ca^{2+} are expressed in meq/L. The classification of irrigation water quality based on SAR is shown in Table 2.

Sodium percentage (%Na) is widely used to assess the suitability of groundwater quality for irrigation purpose (Golekar et al. 2013a). %Na is calculated as follows:

$$Na\% = \frac{(K^+ + Na^+) \times 100}{K^+ + Na^+ + Ca^{2+} + Mg^{2+}} \quad (4)$$

where K^+ , Na^+ , Mg^{2+} and Ca^{2+} are expressed in meq/L. The classification of irrigation water quality based on the %Na is as follows: (1) excellent (<20), (2) good (20–40),

Table 1 Classification of groundwater quality based on CWQI

<i>F</i>	<0.80	0.80–2.50	2.50–4.25	4.25–7.2	>7.2
Water quality	Excellent	Good	Medium	Poor	Extremely poor

Table 2 Classification of irrigation water quality based on SAR

SAR	Description	Water quality
<10	Low sodium water	Excellent
10–18	Medium sodium water	Good
18–26	High sodium water	Permissible
>26	Extremely high sodium water	Unsuitable

(3) permissible (40–60), (4) doubtful (60–80), (5) unsuitable (>80).

The residual sodium carbonate (RSC) is used to identify the hazard impacts of high bicarbonate and carbonate groundwater on the soil. The RSC is calculated using formula (5):

$$RSC = (CO_3^{2-} + HCO_3^-) - (Mg^{2+} + Ca^{2+}) \quad (5)$$

where CO_3^{2-} , HCO_3^- , Mg^{2+} and Ca^{2+} are expressed in meq/L. The quality of irrigation water based on the RSC can be classified as (Golekar et al. 2014): (1) good (<1.25), (2) doubtful (1.25–2.5), (3) unsuitable (>2.5).

Permeability index (PI) is widely used to evaluate the effects on soil permeability of Na^+ , Ca^{2+} , Mg^{2+} and HCO_3^- in groundwater which is long term used for irrigation purposes (Doneen 1964). The PI is computed as follows:

$$PI = \frac{Na^+ + \sqrt{HCO_3^-}}{Na^+ + Ca^{2+} + Mg^{2+}} \times 100 \quad (6)$$

where Na^+ , Mg^{2+} , Ca^{2+} and HCO_3^- are expressed in meq/L. Based on the PI values, irrigation water quality is classified into three classes: excellent (class I), acceptable (class II) and unsuitable (class III).

Health risk assessment

Health risk assessment provides an important reference for groundwater environmental protection and management (Wu and Sun 2016). Human is usually exposed to contaminants through ingestion, inhalation and skin contact. Normally, drinking water intake and skin contact are the main pathways to pose health risks to human for groundwater. Many studies have shown that the health risks of contaminated groundwater through skin contact can be ignored in comparison with the drinking water intake (Liu et al. 2011). Due to inadequate valuable data for the assessment of the health risk caused by skin contact, therefore, this study only evaluated the health risks from

drinking water intake pathway using the models proposed by the Ministry of Environmental Protection of the PR China (2014). In this study, NO_3^- , NO_2^- , F^- , Fe, Mn, Zn, Ba^{2+} , Cr^{6+} and As were used as the parameters for health risk assessment. The health risks caused by drinking water intake can be calculated as follows:

The non-carcinogenic risk through drinking water intake is calculated by formulas (7) and (8):

$$Intake_{oral} = \frac{C_w \times IR \times EF \times ED}{BW \times AT} \quad (7)$$

$$HQ_{oral} = \frac{Intake_{oral}}{RfD_{oral}} \quad (8)$$

where $Intake_{oral}$ represents the average daily exposure dose through ingestion of groundwater [mg/(kg day)], C_w is the concentration of target pollutants in groundwater (mg/L), IR represents groundwater ingestion rate (L/d, IR = 1.5 L/day for adults and 0.7 L/day for children in this study), EF represents the exposure frequency (days/year, EF = 365 days/year), ED represents the exposure duration (years, ED = 30 years for adults and 12 years for children), BW represents the average body weight (kg, BW = 56.8 kg for adults and 15.9 kg for children in this study), and AT represents average exposure time (days, AT = 10,950 days for adults and 4380 days for children), HQ_{oral} and RfD_{oral} represent the hazard quotient and reference dosage, respectively, for non-carcinogenic pollutants through drinking water intake [mg/(kg d)]. In the present study, the RfD_{oral} values of NO_3^- , NO_2^- , F^- , Fe, Mn, Zn, Ba^{2+} , Cr^{6+} and As are 1.6, 0.1, 0.04, 0.3, 0.14, 0.3, 0.2, 0.003 and 0.0003 mg/(kg d), respectively.

According to the health risk assessment standard recommended by the Ministry of Environmental Protection of the PR China (2014), the acceptable limit of HQ is 1. $HQ > 1$ means the non-carcinogenic risk is beyond the acceptable limit. Cr^{6+} and As can also cause carcinogenic risks in addition to non-carcinogenic risks. The carcinogenic risks caused by Cr^{6+} and As through drinking water intake are expressed as (Ministry of Environmental Protection of the PR China 2014):

$$CR_{oral} = Intake_{oral} \times SF_{oral} \quad (9)$$

In this formula, CR indicates the carcinogenic risk. CR value of more than 1×10^{-6} is considered harmful for human health. SF represents the slope factor of carcinogenic pollutants (mg/(kg d), SF = 0.5 mg/(kg d) for Cr^{6+} and 1.5 mg/(kg d) for As). The exposure duration (ED) for carcinogenic risk is 70 years for adults and children.

Results and discussion

Groundwater chemistry

General hydrogeochemical characteristics

The results of statistical analysis of all collected groundwater samples in the study area are given in Table 3. pH is an important hydrogeological parameter indicating whether groundwater is suitable for drinking (Li and Qian 2011). The national standards prescribe that the acceptable pH range for drinking water is 6.5–8.5. As shown in Table 3, the pH is in the range of 7.34–8.47 with a mean of 7.51, which suggests that the groundwater is slightly alkaline in nature over the study area. The pH values of all the samples are within the acceptable limits. As a significant index for analyzing groundwater quality, national standards stipulate that the maximum of EC cannot exceed 2500 $\mu\text{s}/\text{cm}$ for drinking purposes. The EC concentration in the study area ranges from 239 to 1907 $\mu\text{s}/\text{cm}$ with an average of 576.92 $\mu\text{s}/\text{cm}$, indicating that all groundwater locations are within the prescribed limits.

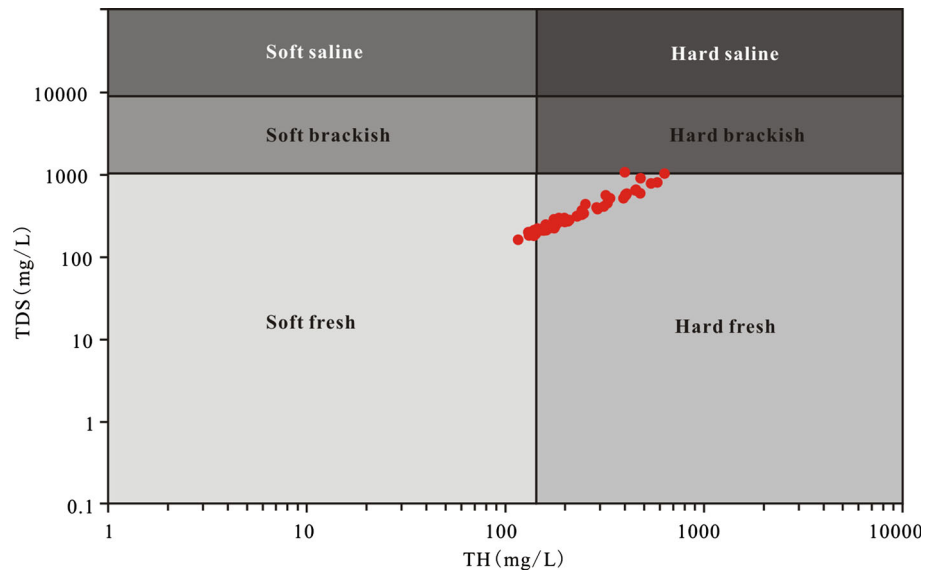
TDS is usually used to ascertain whether groundwater is suitable for human consumption (Li et al. 2014c). Groundwater with TDS < 1000 mg/L is considered suitable for drinking. The level of TDS in the study area ranges from 164.90 to 1097.00 mg/L with a mean of 369.58 mg/L, demonstrating that TDS can meet the requirements of drinking water after mixing. Only two groundwater samples (YL33 and YL57) exceed the permissible limit, and they are observed near the sewage discharge in the downstream of the Yuxi River, which indicates that domestic wastewater entering the aquifer through the unsaturated zone is the main cause of deterioration of groundwater quality. TH represents the sum of the evaporites (Ca^{2+} and Mg^{2+}) dissolved in groundwater. The TH in the study area is in the range of 116.3–636.30 mg/L with a mean of 246.25 mg/L. National standards set 450 mg/L as the allowable limit for TH in groundwater for drinking purposes. Seven groundwater samples (11.48% of all collected samples) are classified as extremely hard water ($\text{TH} > 450$ mg/L) which are unfit for drinking. These samples are mainly distributed in the valley of Yuxi River and Liuqian River, suggesting that these two contaminated

Table 3 Statistics of physiochemical parameters of groundwater samples

Index	Sample number	Unit	Min	Max	Mean	SD	Standard limits	NSES	% of SES
PH	61	–	7.34	8.47	7.51	0.15	6.5–8.5	N	N
EC	61	$\mu\text{s}/\text{cm}$	239.00	1907.00	576.92	356.73	2500	N	N
TDS	61	mg/L	164.90	1097.00	369.58	220.34	1000	2	3.28
TH	61	mg/L	116.30	636.30	246.25	127.86	450	7	11.48
K^+	61	mg/L	0.69	51.30	2.26	6.45	–	–	–
Na^+	61	mg/L	8.95	226.00	32.66	33.65	200	1	1.64
Ca^{2+}	61	mg/L	26.10	163.90	65.07	30.49	200	N	N
Mg^{2+}	61	mg/L	5.62	77.97	20.33	16.48	150	N	N
Cl^-	61	mg/L	2.79	358.90	29.35	51.40	250	1	1.64
SO_4^{2-}	61	mg/L	10.36	238.30	46.38	40.30	250	N	N
HCO_3^-	61	mg/L	143.90	558.40	242.63	99.19	–	–	–
COD	61	mg/L	0.60	3.48	1.21	0.64	3	1	1.64
H_2SiO_3^-	61	mg/L	27.20	35.67	20.78	4.34	–	–	–
NO_3^- -N	61	mg/L	ND	107.48	8.06	17.33	20	5	8.20
NO_2^- -N	61	mg/L	0.00000	0.00487	0.00062	0.00100	0.02	N	N
F^-	61	mg/L	0.34	1.10	0.25	0.22	1	1	1.64
Fe	61	mg/L	ND	5.74	0.53	1.01	0.3	20	32.79
Mn	61	mg/L	ND	1.57	0.14	0.30	0.1	18	29.51
Zn	61	mg/L	ND	0.12	0.02	0.017	1	N	N
Ba^{2+}	61	mg/L	0.027	0.340	0.11	0.077	1	N	N
Cr^{6+}	61	mg/L	ND	0.008	0.00064	0.002	0.05	N	N
As	61	mg/L	ND	0.039	0.0027	0.006	0.01	3	4.92

“–” no value, *SD* standard deviation, *ND* not detected, *NSES* numbers of samples exceeding the standards, *% of SES* % of samples exceeding the standards

Fig. 2 Groundwater quality classification based on TDS and TH



rivers have severely affected the quality of groundwater (Zhu 2012). TDS and TH are often combined to make a simple classification of groundwater quality (Brindhya et al. 2016). As shown in Fig. 2, a total of thirteen samples (21.34% of all samples) are classified as soft fresh water type. Forty-six groundwater samples (75.41% of all samples) fall in hard fresh water type, and the remaining (only two samples) are hard brackish water type.

K^+ in groundwater is one of the essential trace elements to maintain human health (He and MacGregor 2008). In the study area, the level of K^+ ranges from 0.69 to 51.3 mg/L, with a mean of 2.26 mg/L. Na^+ in the total collected samples is in the range of 8.95–226.00 mg/L with an average of 32.66 mg/L and a standard deviation of 33.65. National standards stipulate that the permissible level of Na^+ for drinking is 200 mg/L. One groundwater sample (YL57) exceeds the permissible limit. This sample is located in the downstream area of Yuxi River, suggesting that the polluted river has a certain impact on the quality of groundwater. Ca^{2+} and Mg^{2+} are also necessary for humans, but excessive intake will have negative impacts on human health. In this study, Ca^{2+} is in the range of 26.10–163.90 mg/L with an average of 65.07 mg/L, signifying that all concentrations are within the acceptable limit. The Mg^{2+} concentration ranges between 5.62 and 77.97 mg/L with a mean of 20.33 mg/L. These concentrations are acceptable for drinking. Overall, the abundance of cations based on the average values is as follows: $Ca^{2+} > Na^+ > Mg^{2+} > K^+$. For anions, the concentrations of Cl^- , SO_4^{2-} and HCO_3^- are in the range of 2.79–358.90, 10.36–238.30 and 143.90–558.40 mg/L, respectively. National drinking water quality standards stipulate that the acceptable limit of Cl^- and SO_4^{2-} is 250 mg/L. In the study area, only one sample (YL57)

exceeds the acceptable limit for Cl^- and all samples are within the limit for SO_4^{2-} . Based on mean concentrations, the abundance of anions is $HCO_3^- > SO_4^{2-} > Cl^-$.

NO_3-N is an effective indicator usually used to measure the extent of groundwater contamination by agricultural activities (Golekar et al. 2013b; Wu et al. 2013a). National standards prescribe that NO_3-N concentration should be less than 20 mg/L in drinking water. In this study, five samples have NO_3-N concentration higher than the standard limit. It is believed that NO_3-N pollution of groundwater in this area is closely related to agricultural activities. Each year, large quantities of fertilizer and pesticide are used to ensure the plant production and a large amount of groundwater is used for irrigation. Soluble NO_3-N can easily reach the aquifer through the vadose zone with sufficient irrigation water infiltration, increasing the concentration of NO_3-N in groundwater.

F^- is an essential trace element for human health, but the long-term intake of excessive fluoride can lead to fluorosis (Adimalla and Venkatayogi 2017; Li et al. 2014a). The WHO standards stipulate that the optimal level of F^- in drinking water should be less than 1.5 mg/L, while the Chinese national standards set the optimal level to be less than 1.0 mg/L. In this study, the concentration of F^- ranges from 0.34 to 1.10 mg/L, with a mean of 0.25 mg/L (Table 3). Only one groundwater sample (YL34) is not suitable for drinking due to the high concentration of F^- . This sample is located in the loess area in the southeast of the study area, indicating that F^- may be contributed by fluorine-containing minerals, such as muscovite, biotite and fluorite (Regional Hydrogeologic Investigation Team of Shaanxi 1980).

Heavy metals such as Fe, Mn, Zn and Ba^{2+} are necessary for humans in trace amount, but excessive intake can

have a negative impact on health (Gao and Chen 2012). As shown in Table 3, the concentrations of Fe, Mn, Zn, Ba^{2+} , Cr^{6+} and As are in the range of 0–5.74, 0–1.57, 0–0.12, 0.027–0.340, 0–0.008 and 0–0.039 mg/L, respectively. All metals except Zn, Ba^{2+} and Cr^{6+} exceed the acceptable limits for drinking water. Twenty samples (32.79% of all samples) exceed the acceptable limit of Fe for drinking purposes, eighteen samples (29.51% of all samples) are higher than the acceptable level for Mn, and three samples exceed the acceptable limit for As. High Fe and Mn concentrations are observed mostly in the desert area of the study area (Fig. 5). Intensive industrial activities may be the main cause of excessive Fe and Mn in groundwater. Besides, slow groundwater runoff (the average hydraulic gradient is 2.05‰) in this area also provides a good environment for the accumulation of soluble Fe and Mn.

Groundwater types

Piper trilinear diagram (Piper 1944) can directly reflect the hydrogeochemical characteristics and types of groundwater. The relative concentrations of the major ions of groundwater samples in the study area are shown in Fig. 3. For cations, almost all the samples are plotted in zones B and D of the left triangle, signifying that the hydrochemical types of groundwater in the study area are mainly the “calcium” and “no dominant” type. For anions, samples are mostly plotted in zone F of the right triangle, indicating that the groundwater type mainly correlates with the “bicarbonate and carbonate” type. This type of groundwater is primarily a result of dissolution of carbonate minerals (Li et al. 2014c). Fifty-eight groundwater samples (more than 95% of all samples) are plotted in zone 2 of the upper diamond, suggesting that HCO_3^- , Ca^{2+} and Mg^{2+} are the predominant ions in the groundwater of the study area. Samples in zones 1 and 4 show that SO_4^{2-} and Cl^- are the major anions, and Na^+ is the predominant cation for the sample in zone 4.

Groundwater chemistry evolution mechanisms

In order to analyze the evolution mechanism of natural water chemistry, Gibbs (1970) designed two semilog diagrams which are now known as the Gibbs diagrams. Although these diagrams were originally applied to the analysis of surface water, they are now also widely used to characterize the formation mechanism of groundwater chemistry (Li et al. 2016d). The main mechanisms are classified into 3 types by the Gibbs diagrams: evaporation dominance, rock dominance and precipitation dominance (Wu et al. 2013b). Two semilog diagrams show the characteristic regions of these three mechanisms: One is the relationship between TDS and $\text{Na}^+(\text{Na}^+ + \text{Ca}^{2+})$, and the

other one is the ratios of TDS with $\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)$. As shown in Fig. 4, all groundwater samples in the study area are plotted in the middle part of the diagrams, suggesting that rock weathering plays a significant role in the evolution of groundwater chemistry. The molar ratio of HCO_3^- to SiO_2 is often used to approximately determine the types of partial minerals involved in water–rock interactions (Kortatsi et al. 2008). When $\text{HCO}_3^-/\text{SiO}_2 < 5$, the chemical constituents of groundwater are mainly derived from the dissolution of silicate minerals; when $\text{HCO}_3^-/\text{SiO}_2 > 10$, the chemical constituents are from the dissolution of carbonate minerals; when $5 < \text{HCO}_3^-/\text{SiO}_2 < 10$, the chemical constituents come from both. In this study, fifty-three groundwater samples (86.89% of all samples) have $\text{HCO}_3^-/\text{SiO}_2$ ratio higher than 10, suggesting that the main constituents of these groundwater samples are contributed by carbonate minerals. The $\text{HCO}_3^-/\text{SiO}_2$ ratio of the remaining samples (13.11% of all samples) ranges from 8.20 to 9.95, indicating that the dissolution of carbonate and silicate minerals is the source of these chemical constituents.

Groundwater quality assessment

Drinking water quality

In the study area, groundwater is a vital source of drinking water for local residents. The overall groundwater quality was evaluated using the CWQI to determine the suitability for human consumption, and the results are presented in Table 4. As shown in Table 4, *F* values of all analyzed samples vary from 0.71 to 7.30, ranging from excellent quality to extremely poor quality. Thirty groundwater samples (49.18% of all samples) are classified as excellent and good-quality water (ranks I and II) which is suitable for various purposes. Twenty-eight samples are of poor-quality water (rank IV), and three samples belong to extremely poor-quality water (rank V). The ranks IV and V account for 45.90 and 4.92% of all collected samples, respectively, indicating that more than half of groundwater samples are not suitable for human consumption. And the common contaminants in these samples are Fe, Mn, TH, Mg^{2+} and $\text{NO}_3\text{-N}$, which are mainly from natural processes, industrial and agricultural activities. The serious pollution is delineated in Fig. 5. As shown in Fig. 5, the samples with poor and extremely poor-quality water are mainly observed in the valley of the Yuxi River, which indicates that the polluted river water into the aquifer is the main reason for the deterioration of groundwater quality. Moreover, as the discharge area, strong evaporation also affects the suitability of groundwater for drinking purpose. The samples with excellent and good quality are mostly distributed in the tributaries of the Yuxi River. In these areas, the

Fig. 3 Piper diagram of groundwater samples in the study area

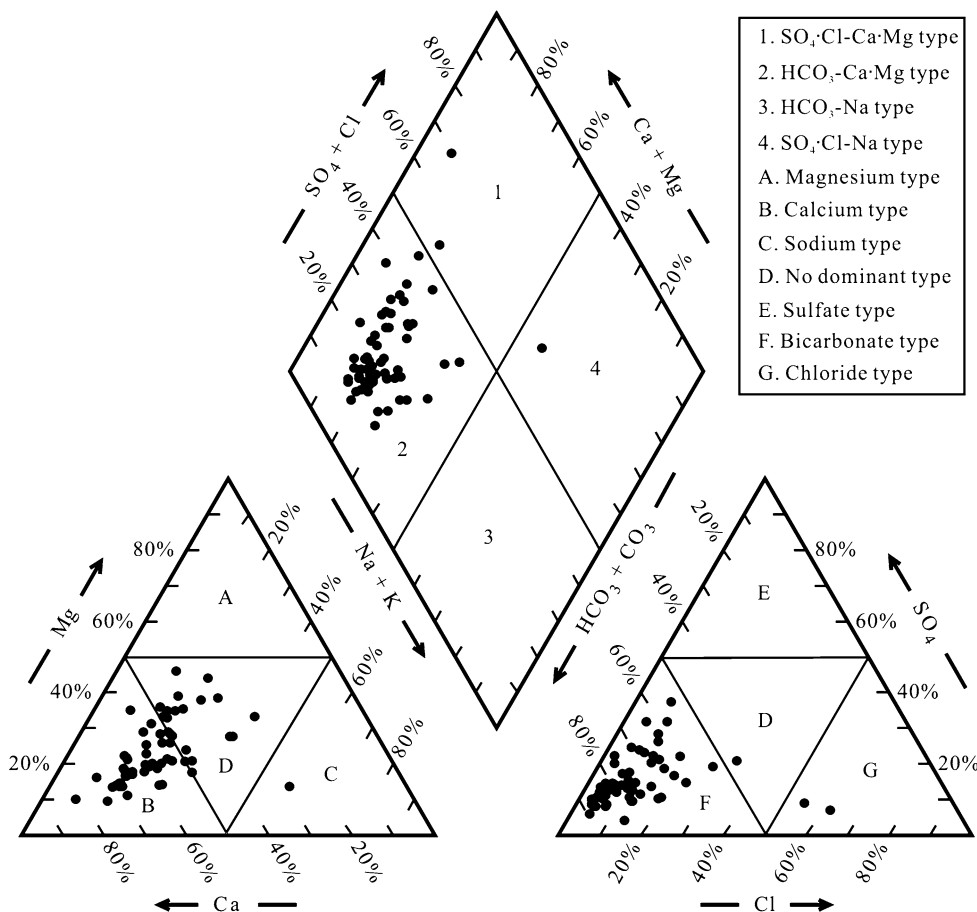
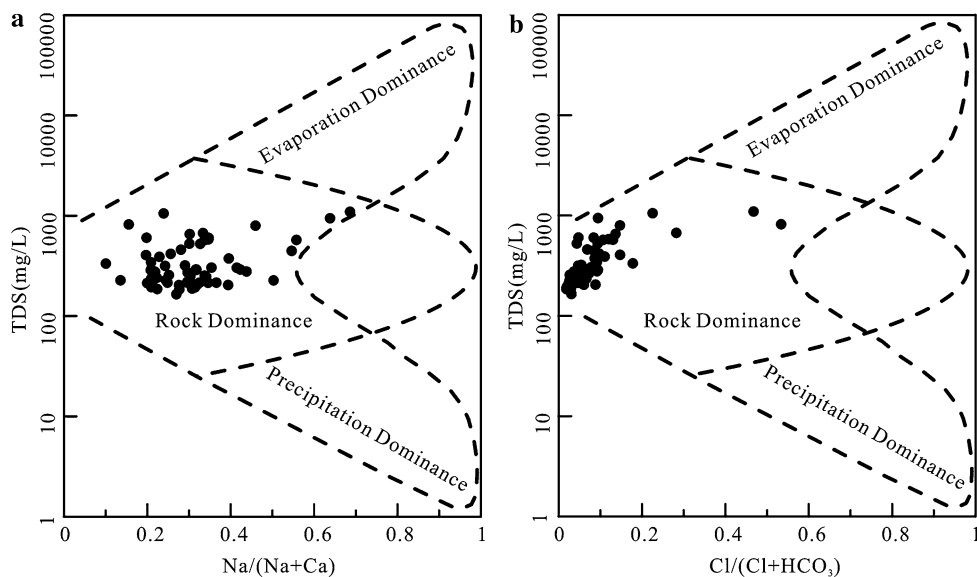


Fig. 4 Gibbs diagrams indicating the major control mechanism of groundwater chemistry



groundwater flow is fast (the average hydraulic gradient is 10‰), indicating a short water–rock interaction time, and therefore less minerals are dissolved in groundwater. In general, groundwater quality in the study area is

unsatisfactory for human consumption. Long-term intake of this groundwater causes serious threats to human health. Therefore, groundwater should be pretreated before being consumed by local residents.

Table 4 Results of groundwater quality evaluation based on CWQI

Sample no.	F	Rank	Sample no.	F	Rank	Sample no.	F	Rank
YL01	2.14	II	YL22	0.72	I	YL43	4.31	IV
YL02	2.14	II	YL23	7.20	IV	YL44	7.10	IV
YL03	4.27	IV	YL24	0.73	I	YL45	4.29	IV
YL04	4.27	IV	YL25	2.15	II	YL46	0.72	I
YL05	2.18	II	YL26	4.27	IV	YL47	2.13	II
YL06	4.26	IV	YL27	7.20	V	YL48	0.71	I
YL07	0.74	I	YL28	2.15	II	YL49	4.27	IV
YL08	2.14	II	YL29	2.19	II	YL50	0.72	I
YL09	0.74	I	YL30	4.40	IV	YL51	0.73	I
YL10	2.15	II	YL31	4.42	IV	YL52	4.27	IV
YL11	0.73	I	YL32	7.18	IV	YL53	4.28	IV
YL12	0.72	I	YL33	7.22	V	YL54	4.38	IV
YL13	2.13	II	YL34	4.43	IV	YL55	2.22	II
YL14	2.16	II	YL35	7.14	IV	YL56	7.13	IV
YL15	0.73	I	YL36	7.14	IV	YL57	7.30	V
YL16	0.71	I	YL37	4.37	IV	YL58	0.73	I
YL17	7.20	IV	YL38	2.18	II	YL59	0.74	I
YL18	2.18	II	YL39	4.29	IV	YL60	0.71	I
YL19	7.18	IV	YL40	4.26	IV	YL61	4.31	IV
YL20	4.34	IV	YL41	0.71	I			
YL21	2.14	II	YL42	4.27	IV			

Irrigation water quality

Groundwater in the study area is also extracted for irrigation in addition to human consumption. Therefore, it is necessary to perform irrigation water quality assessment in order to determine its safety to soil and plants. Many scholars often use the salinity and alkalinity of groundwater to determine its suitability for agricultural irrigation (Thilagavathi et al. 2012). EC is an effective parameter to measure salinity. Generally, groundwater with EC less than 2250 $\mu\text{S}/\text{cm}$ will not cause salinity hazard when used for irrigation. As shown in Table 3, EC ranges from 239.00 to 1907.00 $\mu\text{S}/\text{cm}$, with an average of 576.92 $\mu\text{S}/\text{cm}$, indicating that groundwater in the study area is suitable for irrigation. SAR and %Na are often used to quantify the saline/alkali hazards caused by irrigation water. Table 5 shows the SAR values are in the range of 0.27–4.89 with a mean of 0.86, signifying an excellent groundwater quality for irrigation. %Na varies from 8.30 to 57.97 with an average of 21.25, suggesting the suitability of groundwater for irrigation. Groundwater used for irrigation in the study area will not induce saline/alkali hazards. Groundwater with RSC higher than 2.25 is considered unsuitable for irrigation. In this study, RSC values are observed in the range of -9.27 to 0.74 meq/L with a mean of -0.97 meq/L, suggesting that all the samples are suitable for agricultural use. Long-term use of such groundwater for irrigation may not threaten the health of soil and plants.

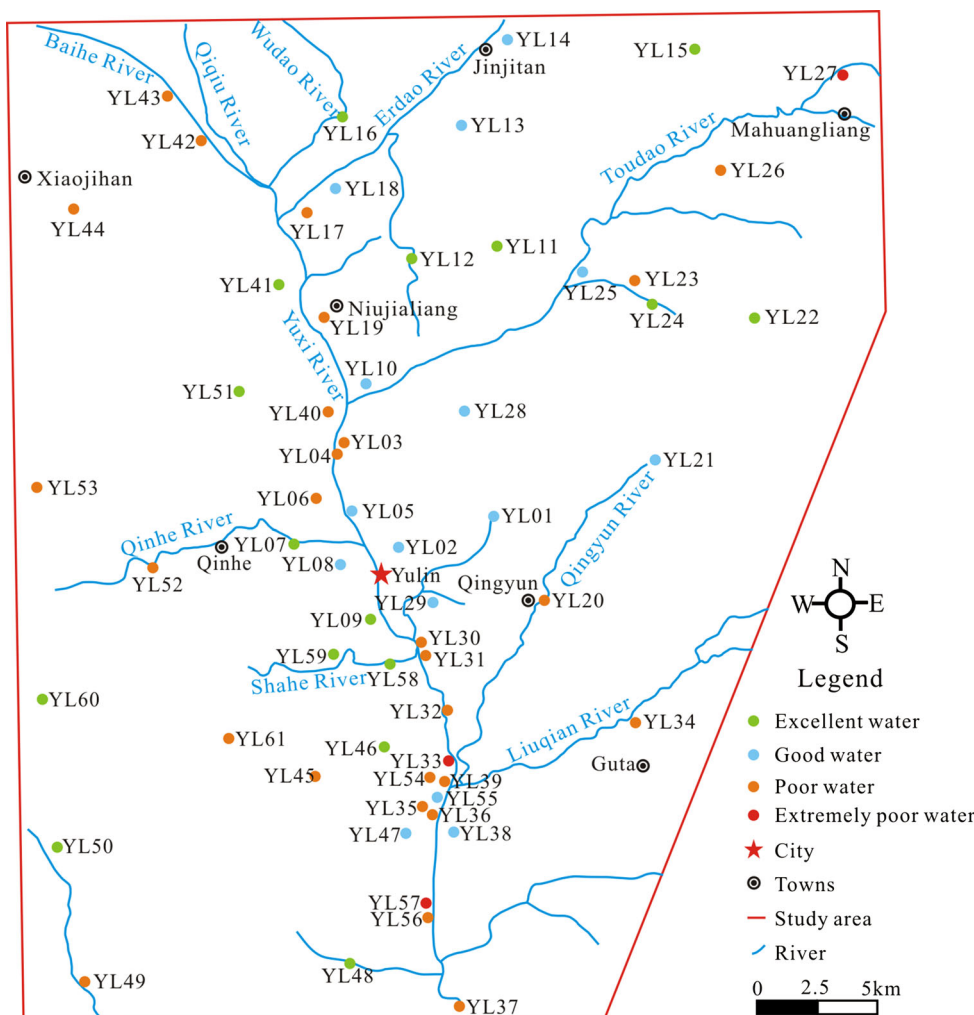
The US salinity diagram (Richards 1954) and the Wilcox (1948) diagram are widely used to evaluate the suitability of groundwater for irrigation purpose. As shown in Fig. 6a, forty-seven samples fall in C1S1 and C2S1, signifying an excellent and good groundwater quality for irrigation. Fourteen samples are plotted in C3S1 and one sample in C3S2, indicating that the groundwater is low alkalinity and high salinity which is acceptable for irrigation. According to the Wilcox diagram (Fig. 6b), sixty groundwater samples are plotted in zones of “excellent to good” and “good to permissible,” indicating the suitability of groundwater for irrigation. Only one sample is observed in “permissible to doubtful” zone with %Na less than 60, suggesting that there would be no sodium hazard if used for irrigation. According to the PI values, twenty-one samples (34.43% of all samples) are observed in class I and forty (65.57% of all samples) in class II (Fig. 7), suggesting that all groundwater samples are suitable for irrigation.

Overall, the long-term use of groundwater in the study area for irrigation may not induce soil salinization and may not affect soil permeability and plant growth.

Health risk assessment

The health risks of non-carcinogens (NO_3^- , NO_2^- , F^- , Fe, Mn, Zn and Ba^{2+}) and carcinogens (Cr^{6+} and As) for adults and children through drinking water intake were assessed using the approach described in the present study.

Fig. 5 Results of groundwater quality evaluation based on CWQI



The assessment results for adults and children are shown in Tables 6 and 7, respectively. For adults, the greatest non-carcinogenic risk through drinking water intake (HQ_{oral}) is caused by NO_3^- , ranging from 0.00 to 7.86 with a mean of 0.59. And As contributes the second non-carcinogenic risk, with a mean of 0.24. Moreover, NO_2^- contributes the least non-carcinogenic risk, with the maximum value of 4.23×10^{-3} . As shown in Fig. 8a, NO_3^- is the largest contributor to the total non-carcinogenic risk (53.99% of total non-carcinogenic risk), followed by As (22.07% of total non-carcinogenic risk) and F^- (15.11% of total non-carcinogenic risk). The remaining contaminants (NO_2^- , Fe, Mn, Zn, Ba^{2+} and Cr^{6+}) contribute only 8.83% of the total non-carcinogenic risk, signifying that NO_3^- , As and F^- are the most influential factors to the health of adults. The order of non-carcinogenic risk is $NO_3^- > As > F^- > Fe > Mn > Ba^{2+} > Cr^{6+} > Zn > NO_2^-$. For children, the greatest contributor to non-carcinogenic risks is also NO_3^- , ranging within 0.00–13.10 with a mean of 0.98 which is almost 1.67 times than that for adults. The order of non-carcinogenic risk for children is the same as

that for adults: $NO_3^- > As > F^- > Fe > Mn > Ba^{2+} > Cr^{6+} > Zn > NO_2^-$ (Fig. 8c). Fe and Mn are the most common metal contaminants in the groundwater of the study area, induced by the natural processes and industrial activities. However, Fe and Mn contribute only 4.31 and 2.37% of the total non-carcinogenic risk, respectively, to adults and children. The reason is that Fe and Mn are essential trace elements in human body and are harmful only in the long-term intake of excessive concentration. The average hazard quotient through drinking water intake (HQ_{oral}) for adults and children is 1.09 and 1.82, respectively, indicating that children in the study area are more vulnerable to contaminants than adults. In general, adults and children in the study area face high non-carcinogenic risk.

As indicated in Tables 6 and 7, the carcinogenic risk (CR_{oral}) caused by As is in the range of 0.00– 1.54×10^{-3} with an average of 1.08×10^{-4} for adults; risk (CR_{oral}) from Cr^{6+} ranges from 0.00 to 1.06×10^{-4} with an average of 8.44×10^{-6} , suggesting that the health risk caused by As is larger than Cr^{6+} (Fig. 8b). The total

Table 5 Results of irrigation water quality evaluation based on SAR, %Na and RSC

Sample no.	SAR	%Na	RSC (meq/L)	Sample no.	SAR	%Na	RSC (meq/L)
YL01	0.63	21.42	0.04	YL33	0.89	15.19	-8.44
YL02	0.53	17.81	-0.38	YL34	2.87	39.76	-0.78
YL03	0.61	19.83	-0.17	YL35	1.23	29.39	0.74
YL04	0.81	24.71	0.01	YL36	1.14	30.78	0.03
YL05	0.93	20.92	-0.92	YL37	2.12	37.36	0.49
YL06	0.47	17.76	-0.27	YL38	0.87	24.72	-0.27
YL07	0.70	17.29	-1.05	YL39	1.22	32.56	0.05
YL08	0.74	21.18	-0.53	YL40	0.89	26.46	0.03
YL09	0.49	14.64	-1.21	YL41	0.29	10.36	-0.44
YL10	0.63	16.16	-2.33	YL42	0.86	27.13	0.31
YL11	0.73	22.12	-0.25	YL43	0.59	20.13	0.09
YL12	0.50	17.92	-0.28	YL44	0.52	16.90	-0.19
YL13	0.46	15.75	-0.74	YL45	0.65	17.98	-1.25
YL14	0.60	16.19	-1.61	YL46	0.49	18.99	0.03
YL15	0.39	13.87	-0.40	YL47	0.70	23.53	-0.15
YL16	0.57	17.03	-0.10	YL48	0.57	20.14	-0.01
YL17	0.78	15.35	-0.47	YL49	0.56	18.50	-0.05
YL18	0.71	21.81	-0.20	YL50	0.52	16.61	-0.74
YL19	0.94	18.60	-5.21	YL51	0.53	17.73	-0.08
YL20	0.86	18.03	-1.28	YL52	0.27	8.30	-2.37
YL21	0.95	28.36	0.32	YL53	0.49	16.80	-0.03
YL22	0.44	15.86	-0.15	YL54	1.10	21.95	-1.64
YL23	1.21	23.19	-2.76	YL55	1.12	23.97	-1.51
YL24	0.50	15.21	-1.10	YL56	0.94	26.20	-0.30
YL25	0.65	21.24	0.05	YL57	4.89	57.97	-1.38
YL26	0.54	19.08	0.10	YL58	0.80	21.35	-0.08
YL27	0.46	8.85	-9.27	YL59	0.84	27.96	0.05
YL28	0.63	19.36	-0.44	YL60	0.42	15.46	0.02
YL29	1.81	36.55	-0.56	YL61	0.65	15.86	-1.29
YL30	1.16	22.66	-1.42	Min	0.27	8.30	-9.27
YL31	1.41	23.26	-3.02	Max	4.89	57.97	0.74
YL32	0.72	14.46	-4.22	Mean	0.86	21.25	-0.97

carcinogenic risk (CR_{total}) for adults ranges from 0.00 to 1.54×10^{-3} with a mean of 1.17×10^{-4} , indicating that the risk is almost two orders of magnitude higher than the recommended level (1×10^{-6}) of the Ministry of Environmental Protection of the PR China (2014). For children, As contributes more risk (58.80% of the total carcinogenic risk) than Cr^{6+} (41.20% of the total carcinogenic risk) (Fig. 8d), because the average concentration of As in groundwater is higher than Cr^{6+} . The total carcinogenic risk (CR_{total}) for children is in the range of 0.00 to 1.14×10^{-3} with an average of 1.37×10^{-4} , signifying that the total carcinogenic risks (CR_{total}) of As and Cr^{6+} exceed the acceptable limit (1×10^{-6}). Therefore, the groundwater in the study area needs pretreatment before being consumed by local residents.

At present, with the rapid development of agriculture and industry, groundwater pollution is becoming more and more serious, causing various diseases such as lung, prostate and bladder cancer (Golekar et al. 2013c). Therefore, many similar groundwater risk assessment researches have been reported in China and other countries in the world (Cai et al. 2015; Giri and Singh 2015; Navoni et al. 2014; Ni et al. 2009; Su et al. 2013; Yang et al. 2012). In order to better understand the health risk of groundwater pollution in the study area, the health risks in the loess area of Northwest China are compared (Table 8).

Li et al. (2016c) performed a detailed study on health risk of groundwater contamination for local residents by direct ingestion in the Weining plain, Northwest China. They found that the hazard quotient through drinking water intake (HQ_{oral})

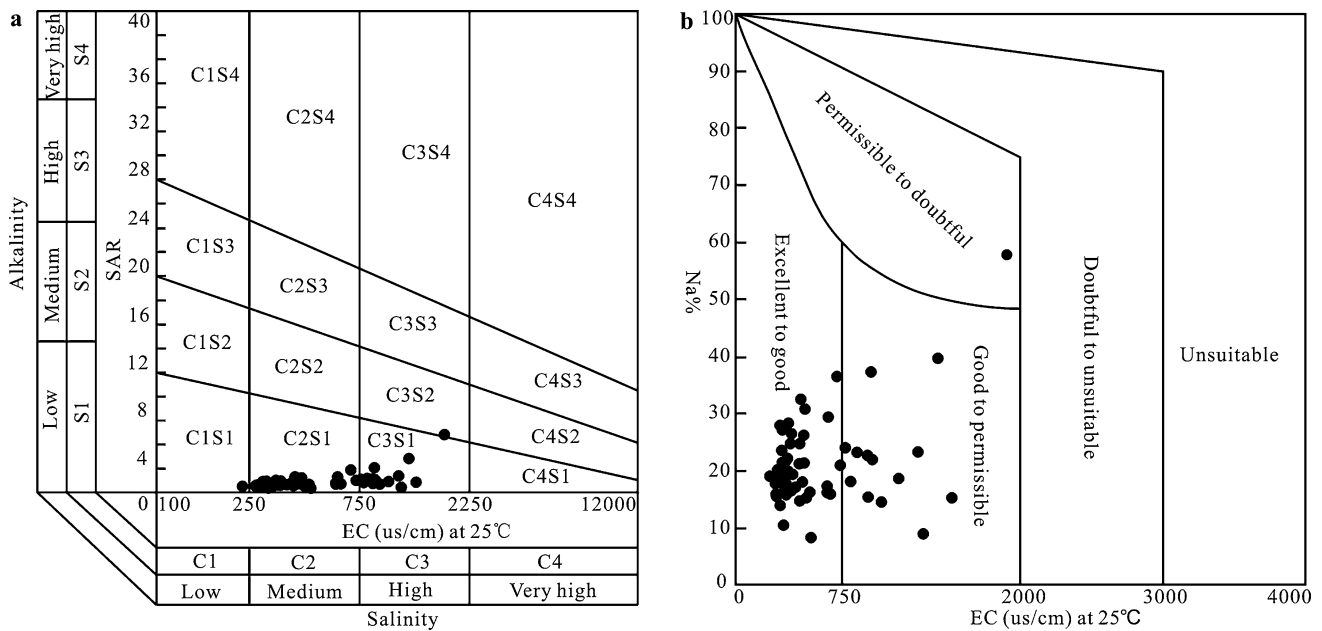


Fig. 6 Evaluation of irrigation water quality based on sodium and salinity hazard

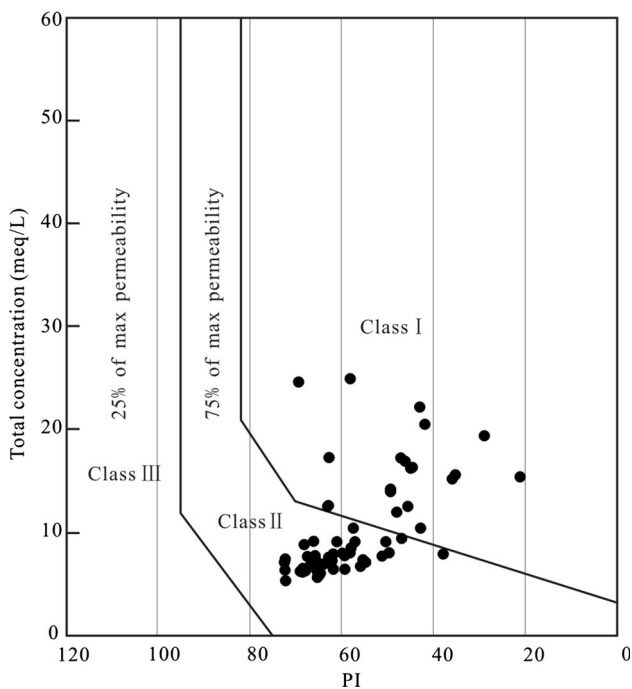


Fig. 7 Evaluation of irrigation water quality based on PI

ranged from 0.35 to 2.94 with an average value of 1.38, and the total carcinogenic risk (CR_{total}) of As and Cr^{6+} was between 1.06×10^{-5} and 7.53×10^{-4} with an average of 5.15×10^{-5} , indicating that the carcinogenic risk was much greater in the study area. Ni et al. (2010) assessed the health risk caused by ingestion of groundwater in Mingshan County, a city in Northwest China. They found that the non-carcinogenic risk was in the range of 0.07438–3.69643 with a mean of

1.44500, and the carcinogenic risk ranged from 1.0×10^{-5} to 2.2×10^{-4} with an average of 1.4×10^{-5} . This suggests that the carcinogenic risk of groundwater pollution in the study area is higher than that in Mingshan County. Wei et al. (2008) assessed the health risk induced through drinking pathway in Yinchuan City, Northwest China. They found the carcinogenic risk was between 2.14×10^{-5} and 8.47×10^{-5} , and the average human health risk was 5.48×10^{-5} . The carcinogenic risk in this study is twice higher than that in Yinchuan City, indicating that carcinogenic pollutants have more negative influences on human health in the study area. Similarly, in other loess areas of Northwest China, many studies on the health risks associated with groundwater consumption also show that the present study area is among the most risky areas (Li and Qian 2011; Li et al. 2014c; Su et al. 2016, 2017; Wu et al. 2017). Therefore, urgent action should be taken to guarantee the safety of drinking water for local residents.

Conclusions

In the present study, sixty-one groups of groundwater samples were collected and twenty-two physiochemical parameters were analyzed. Statistical analysis and Piper diagrams were applied to characterize the general groundwater chemistry. Gibbs diagrams were used to study the formation mechanisms of groundwater chemistry. CWQI was used to assess overall groundwater quality; EC, SAR, %Na, RSC and PI were applied to assess the suitability of groundwater for irrigation purposes. The health

Table 6 Calculated non-carcinogenic and carcinogenic health risks for adults through drinking water intake, year⁻¹

Sample	HQ _{oral}										CR _{oral}		HQ _{total}	CR _{total}
	NO ₃ ⁻	NO ₂ ⁻	F ⁻	Fe	Mn	Zn	Ba ²⁺	Cl ⁶⁺	As	As	Cl ⁶⁺	As		
YL01	0.21	2.54E-03	0.22	0.00	0.00	1.85E-03	1.41E-02	4.40E-02	0	6.60E-05	0.00	0.50	6.60E-05	
YL02	0.33	2.32E-03	0.21	0.00	0.00	1.41E-03	1.44E-02	4.40E-02	0.18	6.60E-05	7.92E-05	0.78	1.45E-04	
YL03	0.29	0.00	0.26	5.39E-02	3.02E-03	2.29E-03	4.13E-02	0.00	0.00	0.00	0.00	0.65	0.00	
YL04	0.07	0.00	0.20	2.98E-02	9.24E-03	1.14E-03	7.13E-03	0.00	0.44	0.00	1.98E-04	0.75	1.98E-04	
YL05	0.63	0.00	0.25	1.06E-03	1.70E-03	1.41E-03	3.35E-02	0.00	0.09	0.00	3.96E-05	1.01	3.96E-05	
YL06	0.00	0.00	0.07	1.72E-02	2.07E-02	1.23E-03	5.41E-03	0.00	0.00	0.00	0.00	0.11	0.00	
YL07	0.10	0.00	0.15	3.35E-03	1.13E-03	1.85E-03	7.92E-03	0.00	0.26	0.00	1.19E-04	0.52	1.19E-04	
YL08	0.39	0.00	0.13	8.98E-03	3.77E-04	2.11E-03	1.23E-02	0.00	0.18	0.00	7.92E-05	0.72	7.92E-05	
YL09	0.30	0.00	0.07	9.24E-03	2.64E-03	2.82E-03	1.27E-02	0.00	0.35	0.00	1.58E-04	0.75	1.58E-04	
YL10	0.83	0.00	0.07	1.32E-03	3.02E-03	1.32E-03	1.14E-02	0.00	0.35	0.00	1.58E-04	1.27	1.58E-04	
YL11	0.33	1.48E-03	0.07	2.99E-03	0.00	1.32E-03	1.25E-02	0.00	0.18	0.00	7.92E-05	0.59	7.92E-05	
YL12	0.25	0.00	0.22	1.50E-03	0.00	3.08E-03	8.05E-03	0.00	0.18	0.00	7.92E-05	0.66	7.92E-05	
YL13	0.45	0.00	0.18	6.87E-03	5.66E-04	3.43E-03	1.12E-02	0.00	0.09	0.00	3.96E-05	0.75	3.96E-05	
YL14	0.46	1.06E-03	0.11	3.26E-03	7.55E-04	1.67E-03	1.91E-02	0.00	0.00	0.00	0.00	0.59	0.00	
YL15	0.29	3.17E-03	0.13	1.14E-03	0.00	2.02E-03	4.36E-03	0.00	0.26	0.00	1.19E-04	0.69	1.19E-04	
YL16	0.03	0.00	0.12	5.72E-03	3.77E-04	2.73E-03	1.02E-02	0.00	0.00	0.00	0.00	0.17	0.00	
YL17	0.01	1.27E-03	0.00	1.95E-01	1.17E-01	2.02E-03	2.69E-02	0.00	3.43	0.00	1.54E-03	3.79	1.54E-03	
YL18	0.16	0.00	0.20	2.17E-02	1.11E-02	1.85E-03	7.00E-03	0.00	1.06	0.00	4.75E-04	1.46	4.75E-04	
YL19	2.53	4.23E-03	0.20	6.43E-03	1.89E-04	1.85E-03	3.09E-02	0.00	0.00	0.00	0.00	2.78	0.00	
YL20	0.02	0.00	0.32	6.37E-02	1.47E-02	3.87E-03	1.88E-02	0.00	0.00	0.00	0.00	0.44	0.00	
YL21	0.20	3.27E-03	0.33	7.66E-03	7.55E-04	1.67E-03	1.76E-02	6.16E-02	0.18	9.24E-05	7.92E-05	0.79	1.72E-04	
YL22	0.18	0.00	0.00	6.25E-03	1.89E-04	2.73E-03	9.11E-03	0.00	0.18	0.00	7.92E-05	0.38	7.92E-05	
YL23	0.17	0.00	0.21	3.46E-01	4.36E-02	1.94E-03	2.10E-02	0.00	0.26	0.00	1.19E-04	1.06	1.19E-04	
YL24	0.29	1.58E-03	0.07	2.64E-03	0.00	1.58E-03	1.00E-02	0.00	0.26	0.00	1.19E-04	0.64	1.19E-04	
YL25	0.03	0.00	0.22	1.83E-02	7.92E-03	2.82E-03	7.66E-03	0.00	0.79	0.00	3.57E-04	1.08	3.57E-04	
YL26	0.26	0.00	0.16	7.24E-02	6.79E-03	1.76E-03	1.51E-02	0.00	0.00	0.00	0.00	0.52	0.00	
YL27	4.94	7.39E-04	0.28	1.19E-02	7.55E-04	4.05E-03	2.97E-02	0.00	0.00	0.00	0.00	5.26	0.00	
YL28	0.45	0.00	0.13	6.78E-03	5.66E-04	1.32E-03	1.73E-02	0.00	0.00	0.00	0.00	0.61	0.00	
YL29	0.24	0.00	0.46	2.20E-03	1.36E-02	1.85E-03	6.21E-03	0.00	0.00	0.00	0.00	0.73	0.00	
YL30	0.28	0.00	0.30	1.76E-01	2.34E-01	2.38E-03	2.83E-02	0.00	0.18	0.00	7.92E-05	1.20	7.92E-05	
YL31	1.67	7.39E-04	0.20	2.55E-03	2.45E-03	1.32E-03	2.85E-02	0.00	0.18	0.00	7.92E-05	2.08	7.92E-05	
YL32	3.68	2.11E-03	0.37	3.17E-03	1.89E-04	1.06E-02	4.49E-02	0.00	0.00	0.00	0.00	4.11	0.00	
YL33	7.86	4.23E-03	0.00	2.99E-03	0.00	2.38E-03	2.88E-02	0.00	0.00	0.00	0.00	7.89	0.00	
YL34	1.08	2.64E-03	0.73	2.11E-03	1.89E-03	1.41E-03	9.24E-03	0.00	0.00	0.00	0.00	1.82	0.00	
YL35	0.04	0.00	0.25	1.69E-01	2.97E-01	8.80E-04	2.73E-02	0.00	0.35	0.00	1.58E-04	1.13	1.58E-04	

Table 6 continued

Sample	HQ _{oral}		CR _{oral}							HQ _{total}	CR _{total}		
	NO ₃ ⁻	NO ₂ ⁻	F ⁻	Fe	Mn	Zn	Ba ²⁺	Cr ⁶⁺	As			As	
YL36	0.35	0.00	0.26	5.05E-01	4.36E-02	4.23E-03	1.68E-02	0.00	0.53	0.00	2.38E-04	1.71	2.38E-04
YL37	0.54	0.00	0.57	7.66E-03	6.83E-02	1.94E-03	1.43E-02	0.00	0.09	0.00	3.96E-05	1.29	3.96E-05
YL38	0.60	0.00	0.55	1.85E-03	1.89E-04	1.58E-03	2.22E-02	0.00	0.09	0.00	3.96E-05	1.27	3.96E-05
YL39	0.29	0.00	0.13	7.56E-02	1.81E-02	5.11E-03	9.77E-03	0.00	0.44	0.00	1.98E-04	0.97	1.98E-04
YL40	0.03	0.00	0.11	9.86E-03	2.51E-02	2.38E-03	1.00E-02	0.00	0.26	0.00	1.19E-04	0.44	1.19E-04
YL41	0.02	0.00	0.07	6.69E-03	3.77E-04	1.94E-03	3.57E-03	0.00	0.18	0.00	7.92E-05	0.28	7.92E-05
YL42	0.01	0.00	0.07	4.94E-02	4.06E-02	1.76E-03	1.07E-02	0.00	0.26	0.00	1.19E-04	0.44	1.19E-04
YL43	0.02	0.00	0.12	5.59E-02	1.79E-01	0	7.26E-03	0.00	2.02	0.00	9.11E-04	2.40	9.11E-04
YL44	0.00	0.00	0.00	2.00E-01	5.28E-02	2.55E-03	7.66E-03	0.00	0.00	0.00	0.00	0.26	0.00
YL45	0.00	0.00	0.07	5.04E-02	5.02E-02	1.41E-03	7.66E-03	0.00	0.00	0.00	0.00	0.18	0.00
YL46	0.14	0.00	0.00	1.51E-02	1.13E-03	2.38E-03	6.47E-03	7.04E-02	0.18	1.06E-04	7.92E-05	0.41	1.85E-04
YL47	0.22	0.00	0.00	8.80E-03	1.13E-03	1.06E-03	1.60E-02	3.52E-02	0.26	5.28E-05	1.19E-04	0.55	1.72E-04
YL48	0.27	0.00	0.07	2.55E-03	0	2.02E-03	6.47E-03	0.00	0.00	0.00	0.00	0.35	0.00
YL49	0.00	0.00	0.07	8.79E-02	3.51E-02	1.50E-03	5.55E-03	0.00	0.00	0.00	0.00	0.20	0.00
YL50	0.23	0.00	0.00	3.26E-03	5.09E-03	1.58E-03	6.34E-03	0.00	0.00	0.00	0.00	0.25	0.00
YL51	0.27	6.34E-04	0.00	8.80E-03	1.70E-03	1.85E-03	8.71E-03	5.28E-02	0.00	7.92E-05	0.00	0.34	7.92E-05
YL52	1.25	7.39E-04	0.00	5.11E-02	2.26E-03	7.92E-04	6.87E-03	3.52E-02	0.00	5.28E-05	0.00	1.34	5.28E-05
YL53	0.01	0.00	0.07	7.54E-02	2.89E-02	4.40E-04	6.07E-03	0.00	0.00	0.00	0.00	0.19	0.00
YL54	0.19	0.00	0.07	5.35E-02	2.15E-02	9.68E-04	2.65E-02	0.00	0.00	0.00	0.00	0.36	0.00
YL55	1.13	0.00	0.08	1.67E-03	3.77E-04	1.32E-03	2.52E-02	0.00	0.00	0.00	0.00	1.23	0.00
YL56	0.29	0.00	0.13	1.78E-01	3.49E-02	2.11E-03	1.11E-02	0.00	0.35	0.00	1.58E-04	1.00	1.58E-04
YL57	0.14	0.00	0.15	1.32E-01	1.32E-01	2.20E-03	4.37E-02	0.00	0.44	0.00	1.98E-04	1.03	1.98E-04
YL58	0.13	0.00	0.07	2.82E-03	2.64E-03	1.23E-03	9.11E-03	0.00	0.00	0.00	0.00	0.21	0.00
YL59	0.03	0.00	0.17	1.24E-02	2.26E-03	4.84E-03	5.94E-03	0.00	0.18	0.00	7.92E-05	0.40	7.92E-05
YL60	0.13	0.00	0.18	5.46E-03	1.13E-03	1.67E-03	6.73E-03	0.00	0.00	0.00	0.00	0.33	0.00
YL61	0.67	0.00	0.20	7.83E-03	3.73E-02	3.52E-03	1.10E-02	0.00	0.00	0.00	0.00	0.93	0.00
Min	0.00	0.00	0.00	0.00	0.00	0.00	3.57E-03	0.00	0.00	0.00	0.00	0.11	0.00
Max	7.86	4.23E-03	0.73	5.05E-01	2.97E-01	1.06E-02	4.49E-02	7.04E-02	3.43	1.06E-04	1.54E-03	7.89	1.54E-03
Mean	0.59	5.37E-04	0.16	4.71E-02	2.59E-02	2.17E-03	1.51E-02	5.63E-03	0.24	8.44E-06	1.08E-04	1.09	1.17E-04

Table 7 Calculated non-carcinogenic and carcinogenic health risks for children through drinking water intake, year⁻¹

Sample	HQ _{oral}			CR _{oral}					HQ _{total}	CR _{total}			
	NO ₃ ⁻	NO ₂ ⁻	F ⁻	Fe	Mn	Zn	Ba ²⁺	Cl ⁶⁺			As		
YL01	0.35	4.23E-03	0.37	0.00	0.00	3.08E-03	2.36E-02	7.34E-02	0.00	4.40E-04	0	0.83	4.40E-04
YL02	0.55	3.87E-03	0.35	0.00	0.00	2.35E-03	2.40E-02	7.34E-02	0.29	4.40E-04	5.87E-05	1.30	4.99E-04
YL03	0.48	0.00	0.44	8.98E-02	5.03E-03	3.82E-03	6.89E-02	0.00	0.00	0.00	0.00	1.09	0.00
YL04	0.11	0.00	0.33	4.96E-02	1.54E-02	1.91E-03	1.19E-02	0.00	0.73	0.00	1.47E-04	1.26	1.47E-04
YL05	1.05	0.00	0.42	1.76E-03	2.83E-03	2.35E-03	5.59E-02	0.00	0.15	0.00	2.94E-05	1.68	2.94E-05
YL06	0.00	0.00	0.11	2.86E-02	3.46E-02	2.05E-03	9.03E-03	0.00	0.00	0.00	0.00	0.18	0.00
YL07	0.16	0.00	0.24	5.58E-03	1.89E-03	3.08E-03	1.32E-02	0.00	0.44	0.00	8.81E-05	0.87	8.81E-05
YL08	0.65	0.00	0.22	1.50E-02	6.29E-04	3.52E-03	2.05E-02	0.00	0.29	0.00	5.87E-05	1.20	5.87E-05
YL09	0.50	0.00	0.11	1.54E-02	4.40E-03	4.70E-03	2.11E-02	0.00	0.59	0.00	1.17E-04	1.24	1.17E-04
YL10	1.39	0.00	0.11	2.20E-03	5.03E-03	2.20E-03	1.89E-02	0.00	0.59	0.00	1.17E-04	2.11	1.17E-04
YL11	0.55	2.47E-03	0.11	4.99E-03	0.00	2.20E-03	2.09E-02	0.00	0.29	0.00	5.87E-05	0.99	5.87E-05
YL12	0.42	0.00	0.37	2.49E-03	0.00	5.14E-03	1.34E-02	0.00	0.29	0.00	5.87E-05	1.11	5.87E-05
YL13	0.75	0.00	0.31	1.14E-02	9.43E-04	5.72E-03	1.87E-02	0.00	0.15	0.00	2.94E-05	1.25	2.94E-05
YL14	0.76	1.76E-03	0.18	5.43E-03	1.26E-03	2.79E-03	3.19E-02	0.00	0.00	0.00	0.00	0.98	0.00
YL15	0.48	5.28E-03	0.22	1.91E-03	0.00	3.38E-03	7.26E-03	0.00	0.44	0.00	8.81E-05	1.15	8.81E-05
YL16	0.05	0.00	0.20	9.54E-03	6.29E-04	4.55E-03	1.69E-02	0.00	0.00	0.00	0.00	0.28	0.00
YL17	0.02	2.11E-03	0.00	3.25E-01	1.95E-01	3.38E-03	4.49E-02	0.00	5.72	0.00	1.14E-03	6.31	1.14E-03
YL18	0.27	0.00	0.33	3.62E-02	1.86E-02	3.08E-03	1.17E-02	0.00	1.76	0.00	3.52E-04	2.43	3.52E-04
YL19	4.22	7.04E-03	0.33	1.07E-02	3.14E-04	3.08E-03	5.15E-02	0.00	0.00	0.00	0.00	4.63	0.00
YL20	0.03	0.00	0.53	1.06E-01	2.45E-02	6.46E-03	3.13E-02	0.00	0.00	0.00	0.00	0.73	0.00
YL21	0.33	5.46E-03	0.55	1.28E-02	1.26E-03	2.79E-03	2.93E-02	1.03E-01	0.29	6.16E-04	5.87E-05	1.32	6.75E-04
YL22	0.30	0.00	0.00	1.04E-02	3.14E-04	4.55E-03	1.52E-02	0.00	0.29	0	5.87E-05	0.63	5.87E-05
YL23	0.28	0.00	0.35	5.76E-01	7.26E-02	3.23E-03	3.50E-02	0.00	0.44	0	8.81E-05	1.76	8.81E-05
YL24	0.49	2.64E-03	0.11	4.40E-03	0.00	2.64E-03	1.67E-02	0.00	0.44	0	8.81E-05	1.06	8.81E-05
YL25	0.04	0.00	0.37	3.05E-02	1.32E-02	4.70E-03	1.28E-02	0.00	1.32	0	2.64E-04	1.80	2.64E-04
YL26	0.44	0.00	0.26	1.21E-01	1.13E-02	2.94E-03	2.51E-02	0.00	0.00	0.00	0.00	0.86	0.00
YL27	8.23	1.23E-03	0.46	1.98E-02	1.26E-03	6.75E-03	4.95E-02	0.00	0.00	0.00	0.00	8.77	0.00
YL28	0.75	0.00	0.22	1.13E-02	9.43E-04	2.20E-03	2.88E-02	0.00	0.00	0.00	0.00	1.01	0.00
YL29	0.40	0.00	0.77	3.67E-03	2.26E-02	3.08E-03	1.03E-02	0.00	0.00	0.00	0.00	1.21	0.00
YL30	0.46	0.00	0.51	2.93E-01	3.91E-01	3.96E-03	4.71E-02	0.00	0.29	0	5.87E-05	2.00	5.87E-05
YL31	2.78	1.23E-03	0.33	4.26E-03	4.09E-03	2.20E-03	4.75E-02	0.00	0.29	0	5.87E-05	3.46	5.87E-05
YL32	6.14	3.52E-03	0.62	5.28E-03	3.14E-04	1.76E-02	7.48E-02	0.00	0.00	0.00	0.00	6.85	0.00
YL33	13.10	7.04E-03	0.00	4.99E-03	0.00	3.96E-03	4.80E-02	0.00	0.00	0.00	0.00	13.16	0.00
YL34	1.80	4.40E-03	1.21	3.52E-03	3.14E-03	2.35E-03	1.54E-02	0.00	0.00	0.00	0.00	3.04	0.00
YL35	0.06	0.00	0.42	2.81E-01	4.94E-01	1.47E-03	4.56E-02	0.00	0.59	0.00	1.17E-04	1.89	1.17E-04

Table 7 continued

Sample	HQ _{oral}		CR _{oral}							HQ _{total}	CR _{total}		
	NO ₃ ⁻	NO ₂ ⁻	F ⁻	Fe	Mn	Zn	Ba ²⁺	Ci ⁶⁺	As	Ci ⁶⁺	As		
YL36	0.59	0.00	0.44	8.43E-01	7.26E-02	7.04E-03	2.80E-02	0.00	0.88	0.00	1.76E-04	2.86	1.76E-04
YL37	0.91	0.00	0.95	1.28E-02	1.14E-01	3.23E-03	2.38E-02	0.00	0.15	0.00	2.94E-05	2.15	2.94E-05
YL38	1.00	0.00	0.92	3.08E-03	3.14E-04	2.64E-03	3.70E-02	0.00	0.15	0.00	2.94E-05	2.12	2.94E-05
YL39	0.48	0.00	0.22	1.26E-01	3.02E-02	8.51E-03	1.63E-02	0.00	0.73	0.00	1.47E-04	1.61	1.47E-04
YL40	0.05	0.00	0.18	1.64E-02	4.18E-02	3.96E-03	1.67E-02	0.00	0.44	0.00	8.81E-05	0.74	8.81E-05
YL41	0.04	0.00	0.11	1.12E-02	6.29E-04	3.23E-03	5.94E-03	0.00	0.29	0.00	5.87E-05	0.46	5.87E-05
YL42	0.01	0.00	0.11	8.23E-02	6.76E-02	2.94E-03	1.78E-02	0.00	0.44	0.00	8.81E-05	0.73	8.81E-05
YL43	0.03	0.00	0.20	9.32E-02	2.98E-01	0.00	1.21E-02	0.00	3.38	0.00	6.75E-04	4.00	6.75E-04
YL44	0.00	0.00	0.00	3.34E-01	8.81E-02	4.26E-03	1.28E-02	0.00	0.00	0.00	0.00	0.44	0.00
YL45	0.00	0.00	0.11	8.41E-02	8.36E-02	2.35E-03	1.28E-02	0	0.00	0	0	0.29	0
YL46	0.23	0.00	0.00	2.52E-02	1.89E-03	3.96E-03	1.08E-02	1.17E-01	0.29	7.04E-04	5.87E-05	0.68	7.63E-04
YL47	0.37	0.00	0.00	1.47E-02	1.89E-03	1.76E-03	2.66E-02	5.87E-02	0.44	3.52E-04	8.81E-05	0.91	4.40E-04
YL48	0.45	0.00	0.11	4.26E-03	0	3.38E-03	1.08E-02	0.00	0.00	0.00	0.00	0.58	0.00
YL49	0.00	0.00	0.11	1.47E-01	5.85E-02	2.49E-03	9.25E-03	0.00	0.00	0.00	0.00	0.33	0.00
YL50	0.39	0.00	0.00	5.43E-03	8.49E-03	2.64E-03	1.06E-02	0.00	0.00	0.00	0.00	0.42	0.00
YL51	0.44	1.06E-03	0.00	1.47E-02	2.83E-03	3.08E-03	1.45E-02	8.81E-02	0.00	5.28E-04	0.00	0.57	5.28E-04
YL52	2.08	1.23E-03	0.00	8.53E-02	3.77E-03	1.32E-03	1.14E-02	5.87E-02	0.00	3.52E-04	0.00	2.24	3.52E-04
YL53	0.01	0.00	0.11	1.26E-01	4.81E-02	7.34E-04	1.01E-02	0.00	0.00	0.00	0.00	0.31	0.00
YL54	0.32	0.00	0.11	8.92E-02	3.58E-02	1.61E-03	4.42E-02	0.00	0.00	0.00	0.00	0.60	0.00
YL55	1.88	0.00	0.13	2.79E-03	6.29E-04	2.20E-03	4.20E-02	0.00	0.00	0.00	0.00	2.06	0.00
YL56	0.48	0.00	0.22	2.96E-01	5.82E-02	3.52E-03	1.85E-02	0.00	0.59	0.00	1.17E-04	1.66	1.17E-04
YL57	0.23	0.00	0.24	2.19E-01	2.20E-01	3.67E-03	7.29E-02	0.00	0.73	0.00	1.47E-04	1.72	1.47E-04
YL58	0.21	0.00	0.11	4.70E-03	4.40E-03	2.05E-03	1.52E-02	0.00	0.00	0.00	0.00	0.35	0
YL59	0.04	0.00	0.29	2.07E-02	3.77E-03	8.07E-03	9.91E-03	0.00	0.29	0.00	5.87E-05	0.67	5.87E-05
YL60	0.22	0.00	0.31	9.10E-03	1.89E-03	2.79E-03	1.12E-02	0.00	0.00	0.00	0.00	0.56	0.00
YL61	1.11	0.00	0.33	1.31E-02	6.23E-02	5.87E-03	1.83E-02	0.00	0.00	0.00	0.00	1.54	0.00
Min	0.00	0.00	0.00	0.00	0.00	0.00	5.94E-03	0.00	0.00	0.00	0.00	0.18	0.00
Max	13.10	7.04E-03	1.21	8.43E-01	4.94E-01	1.76E-02	7.48E-02	1.17E-01	5.72	7.04E-04	1.14E-03	13.16	1.14E-03
Mean	0.98	8.95E-04	0.27	7.85E-02	4.32E-02	3.62E-03	2.52E-02	9.38E-03	0.40	5.63E-05	8.04E-05	1.82	1.37E-04

Fig. 8 Contributive ratios of different pollutants to health risks, **a** non-carcinogenic risk for adults, **b** carcinogenic risk for adults, **c** non-carcinogenic risk for children and **d** carcinogenic risk for children

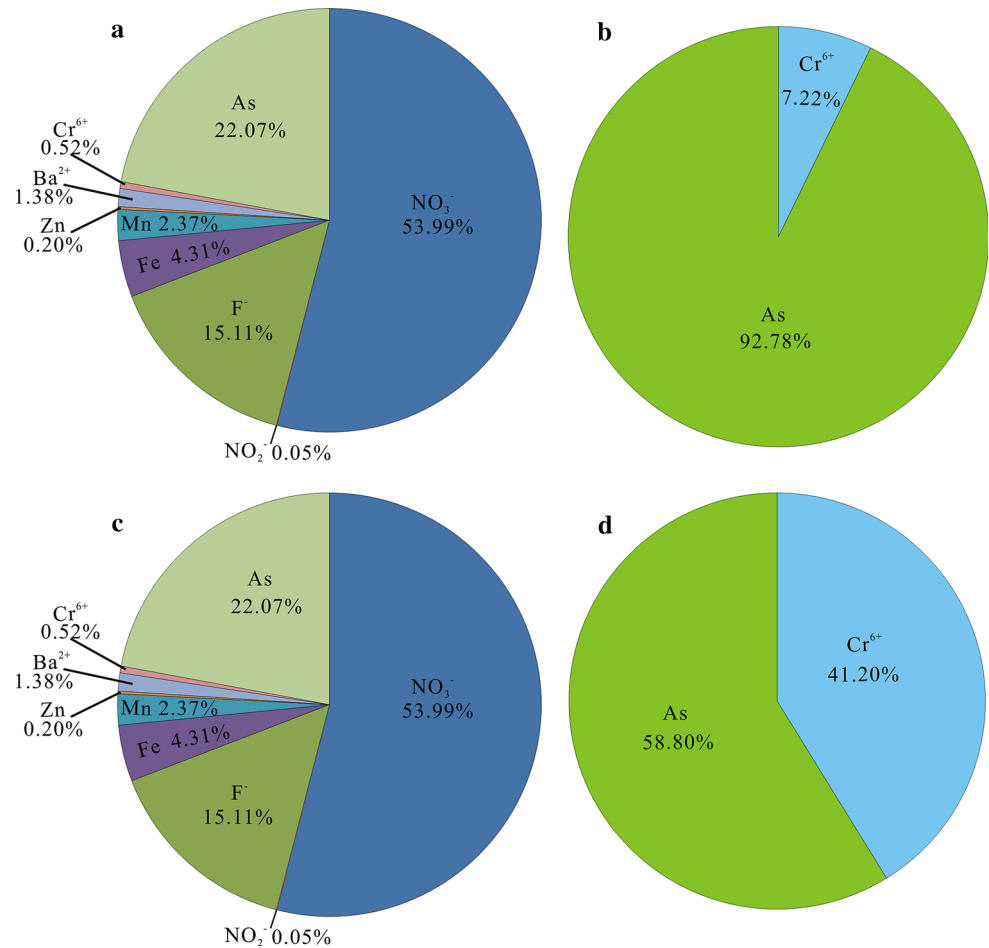


Table 8 Comparison of health risks associated with groundwater consumption between Yulin City and other loess areas of Northwest China

Locations	Non-carcinogenic risk			Carcinogenic risk			References
	Min	Max	Mean	Min	Max	Mean	
Yulin City, Northwest China	0.11	7.89	1.09	0	1.54E-03	1.17E-04	Present study
Weining plain, Northwest China	0.35	2.94	1.38	1.06E-05	7.53E-04	5.15E-05	Li et al. (2016c)
Mingshan County, Northwest China	0.07438	3.69643	1.44500	1.0E-05	2.2E-04	1.4E-05	Ni et al. (2010)
Yinchuan City, Northwest China	–	–	–	2.14E-05	8.47E-05	5.48E-05	Wei et al. (2008)
Shizuishan City, Northwest China	1.60	4.53	3.18	1.96E-05	3.31E-04	7.71E-05	Li and Qian (2011)
Zhongning County, Northwest China	–	–	–	3.62E-05	2.93E-04	8.31E-05	Li et al. (2014c)
Dingbian County, Northwest China	0.22	15.39	3.64	2.94E-07	9.40E-06	1.36E-06	Su et al. (2016)
Shenfu mining area, Northwest China	0	30.45	1.56	–	–	–	Su et al. (2017)
Yinchuan Beijiao water resource, Northwest China	0.1949	1.3730	0.5205	0.3236E-05	1.7721E-04	1.5501E-05	Wu (2014)

Note: “–” no value

risk assessment model recommended by the Ministry of Environmental Protection of the PR China was used to estimate the health risks caused by ingestion of groundwater to adults and children. The following conclusions can be drawn:

1. The pH value of groundwater in the study area varies from 7.34 to 8.47 signifying alkalinity. TDS and TH are in the range of 164.90–1097.00 and 116.3–636.30 mg/L, respectively. The abundance of anions and cations is $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ and

$\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, respectively, which makes the predominant type of groundwater is $\text{HCO}_3\text{-Ca}\cdot\text{Mg}$ type. Gibbs diagrams indicate that rock weathering and water–rock interactions control the formation mechanisms of groundwater chemistry. The main pollutants in groundwater are TH, Mg^{2+} and $\text{NO}_3\text{-N}$, indicating that groundwater in the study area needs to be pretreated before being used for drinking purposes by local residents. Trace elements are necessary for human body, but the excess will have a negative impact on health. Fe, Mn and As contamination occurs in some areas due to natural and anthropogenic factors.

- The assessment result of the overall groundwater quality in the study area based on CWQI shows that 49.18% of the groundwater samples are classified as excellent and good-quality water which is suitable for various purposes. More than half of groundwater samples (50.82% of the samples) are classified as poor and extremely poor-quality water. Fe, Mn, TH, Mg^{2+} and $\text{NO}_3\text{-N}$ are the common contaminants in these samples, which are mainly from natural processes, industrial and agricultural activities. EC, SAR, %Na, RSC, US salinity diagram, Wilcox diagram and PI signify that groundwater in the study area for irrigation will not induce soil salinization and will not affect soil permeability and plant growth.
- Contaminated groundwater in the study area has a negative impact on the health of the local residents through drinking water intake. The total non-carcinogenic risk is in the range of 0.11–7.89 for adults. The non-carcinogenic risk is higher for children, ranging from 0.18 to 13.16. The order of contribution of contaminants to non-carcinogenic risk for adults and children is $\text{NO}_3^- > \text{As} > \text{F}^- > \text{Fe} > \text{Mn} > \text{Ba}^{2+} > \text{Cr}^{6+} > \text{Zn} > \text{NO}_2^-$. The total carcinogenic risks of carcinogens (Cr^{6+} and As) for adults and children range from 0.00 to 1.54×10^{-3} and 0.00 to 1.14×10^{-3} , with averages of 1.17×10^{-4} and 1.37×10^{-4} , respectively, which exceed the permissible level (1×10^{-6}) stipulated by the Ministry of Environmental Protection of the PR China. Hence, effective measures are highly demanded to manage groundwater pollution and reduce the risks to human health.

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