



Groundwater Quality Assessment Using Improved Water Quality Index (WQI) and Human Health Risk (HHR) Evaluation in a Semi-arid Region of Northwest China

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Received: 2 December 2019 / Revised: 10 January 2020 / Accepted: 14 January 2020 / Published online: 22 January 2020
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Abstract

To ensure the safety of drinking water, 51 groundwater samples were collected from a semi-arid area of China and various physicochemical parameters were analyzed. Groundwater quality for drinking purposes along with the associated health risks was assessed using a water quality index (WQI) which was improved using the Criteria Importance Through Inter-criteria Correlation weighting method. The results show that the groundwater was slightly alkaline and the total dissolved solids ranged from 497.26 to 2198.82 mg/L. The ionic dominance pattern was in the order of $K^+ + Na^+ > Ca^{2+} > Mg^{2+} > NH_4^+$ for cations, and $HCO_3^- > SO_4^{2-} > Cl^- > NO_2^- > NO_3^- > CO_3^{2-} > F^-$ for anions, respectively. In the study region, HCO_3^-Na and HCO_3^-Ca-Mg were the dominant water types, followed by the $SO_4-Cl-Na$ type, which are mainly controlled by rock weathering, leaching, and evaporation. 94.12% of the total samples are suitable for drinking; the poor and extremely poor water for human consumption are mainly located in the center and northeast of the study area. The non-carcinogenic health risk for males ranged from 0.0002 to 38.7575, for females 0.0002 to 49.2935, and for children 0.0003 to 84.3167, respectively. The health risk for children was approximately 2.18 times and 1.71 times higher than that for males and females, indicating that children are more susceptible to water contamination. The major pollutants in the study region are nitrite, nitrate, and fluoride. Therefore, the necessary steps to be taken to clean up this highly nitrite-, nitrate-, and fluoride-contaminated groundwater and health risks in this study region.

Keywords Groundwater pollution · Groundwater chemistry · Water quality index (WQI) · CRITIC · Human health risk evaluation

Introduction

Groundwater accounts for about one-third of freshwater consumption globally, which is important for domestic, industrial, and agricultural use, especially in arid and semi-arid areas where water source is scarce and unevenly distributed (Wu et al. 2017; Chen et al. 2018; Li et al. 2018a, b; Zhang et al. 2018). It is reported that more than 1.5 billion people worldwide rely on groundwater for primary

needs (He et al. 2015; Adimalla and Wu 2019). However, with the swift population growth, rapid industrial development, and extensive agricultural activities, groundwater pollution has become a serious problem in many countries and regions (Adimalla et al. 2018, 2019; Li et al. 2017a, 2019a). Groundwater pollutants mainly include inorganic salts, toxic metals, cations (potassium (K^+), sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+})), and anions (chloride (Cl^-), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and sulfate (SO_4^{2-})) (Khanoranga and Khalid 2019). Therefore, groundwater quality issues have become a major concern in the last several decades, and groundwater quality assessment along with health risk evaluation has widely been studied across the globe, including in China, India, and the USA (Qiu 2010; Yu et al. 2011; Li et al. 2018c). Adimalla and Wu (2019) conducted a study on groundwater quality and the related health risk assessment in a semi-arid region of south India and found that the nitrate and fluoride were the

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principal contaminants affecting drinking water safety in the Siddipeta-Vagu (SDV) region. Xu et al. (2019a) investigated the hydrogeochemical characterization of shallow groundwater in the Central-Western Guanzhong Basin, China, and indicated that $\text{HCO}_3\text{-Ca Mg}$ and $\text{HCO}_3\text{-Na}$ are the main hydrochemical facies, controlled by rock weathering, cation exchange, and evaporation. Karakus (2019) evaluated the groundwater quality in Sivas province, Turkey, showing that TDS, NO_3^- , SO_4^{2-} , Cr, and As negatively affect groundwater quality. Li et al. (2019a) studied fluoride in groundwater of a loess aquifer in Tongchuan, China, finding that high-fluoride groundwater is mainly prevalent in the southeast part of the study area. Similar studies in other regions have been carried out by researchers (Kihumba et al. 2016; Rasool et al. 2016; Adimalla and Qian 2019a; Chen et al. 2019; Ganyaglo et al. 2019; He and Wu 2019; Iticescu et al. 2019; Jia et al. 2019; Rezaei et al. 2019; Zhang et al. 2019).

Groundwater researchers have used many methods to assess groundwater quality. Some of these methods include a fuzzy comprehensive assessment method (Wu et al. 2019), Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) (Li et al. 2013a, b; Gorgij et al. 2019), set pair analysis (Tian and Wu 2019; Su et al. 2019; Lu et al. 2019), Hierarchical analysis (Deng et al. 2017), and water quality index (WQI) (Chen et al. 2019; Li et al. 2014a, 2018d, 2019b). The water quality index (WQI) is an efficient tool to assess water quality using various water quality parameters (Abbasi and Abbasi 2012; Chen et al. 2019). The parameters are often weighted according to their importance to water quality. However, a small change in weighting will affect the overall interpretation of water quality (Mukate et al. 2019). To overcome this problem, the Criteria Importance Though Inter-criteria Correlation (CRITIC) method was used to generate relative weights of parameters in this study. The idea is based on the two concepts of standard deviation and the conflict among the different parameters. The CRITIC weighting method also overcomes the shortcomings of conventional information entropy which considers only the effects of the factor variation and ignores the effects of conflicts between factors (Yu et al. 2019). Therefore, combining the CRITIC weighting theory and WQI analysis is reasonable and can take the advantage of the two methods.

The study area is part of the Guanzhong Basin, located at the starting point of the “Silk Road Economic Belt,” and occupies an important position in China’s regional economic pattern (Li et al. 2015; Xu et al. 2019a). The source of drinking water in the study region is mainly groundwater (Luo et al. 2014). In Guanzhong Basin, the groundwater quality is poor in some areas due to the pollution such as high salinity and the presence of other toxic elements (Luo et al. 2014; Li et al. 2014b, 2016a, b; Xu et al. 2019b). Thus, proper assessment and reporting of groundwater quality are

important issues in the study region. The main objectives of this research are to (1) analyze the hydrogeochemical characteristics and hydrochemical facies of the groundwater and their formation mechanisms; (2) appraise the overall groundwater quality for drinking purposes using WQI based on CRITIC weighting, and (3) assess the non-carcinogenic risks via drinking intake and dermal contact pathways for males, females, and children. The study provides essential information for local groundwater quality protection and management, which is helpful for supporting the sustainable development of drinking water in the study region and establishing a long-term harmonious relationship among humans, society, and the environment.

Materials and Methods

Study Area

The study area ($34^\circ 15'–34^\circ 45' \text{ N}$, $109^\circ 23'–109^\circ 45' \text{ E}$) is a part of the Guanzhong Basin (Fig. 1), where groundwater is one of the main water supply sources. Lei and Ju (2008) and Zhang (2009) reported that the Weinan City drinking water was unsafe and the urban area groundwater was over-exploited (Zhang 2017). The southern part of study area is the Qinling Mountains and the loess platform, with an altitude of 600–2400 m, while the central and northern parts are the Weihe Plain, with an altitude of 330–600 m. The study region is geographically located in warm temperate semi-humid and semi-arid monsoon climate region (Xu et al. 2019b) with an average annual temperature of 13.6°C , an average of 2200–2500 h annual daylight, and a frost-free period of 199–255 days. The annual average rainfall in this area is about 600 mm and the annual average evaporation rate ranges between 1000 and 1200 mm (Xu et al. 2019b).

Geologically, the study region was mainly occupied by the Quaternary alluvial rock group of the alluvial fan and the Quaternary aeolian rock group of the loess plateau. The groundwater in the study area is mainly loose rock pore water. The groundwater level is shallow and varies from 14 to 37 m below the ground level with good recharge conditions. The recharge of groundwater mainly includes rainfall infiltration replenishment, irrigation infiltration recharge, and recharge of Wei River. In addition, the discharge of groundwater mainly includes evaporation and exploiting and the runoff direction of groundwater generally flows from west to east.

Sampling and Analysis

A total of fifty-one phreatic samples were collected in study area from existing hand pumps and bore wells using thoroughly prewashed polyethylene bottles. The samples were

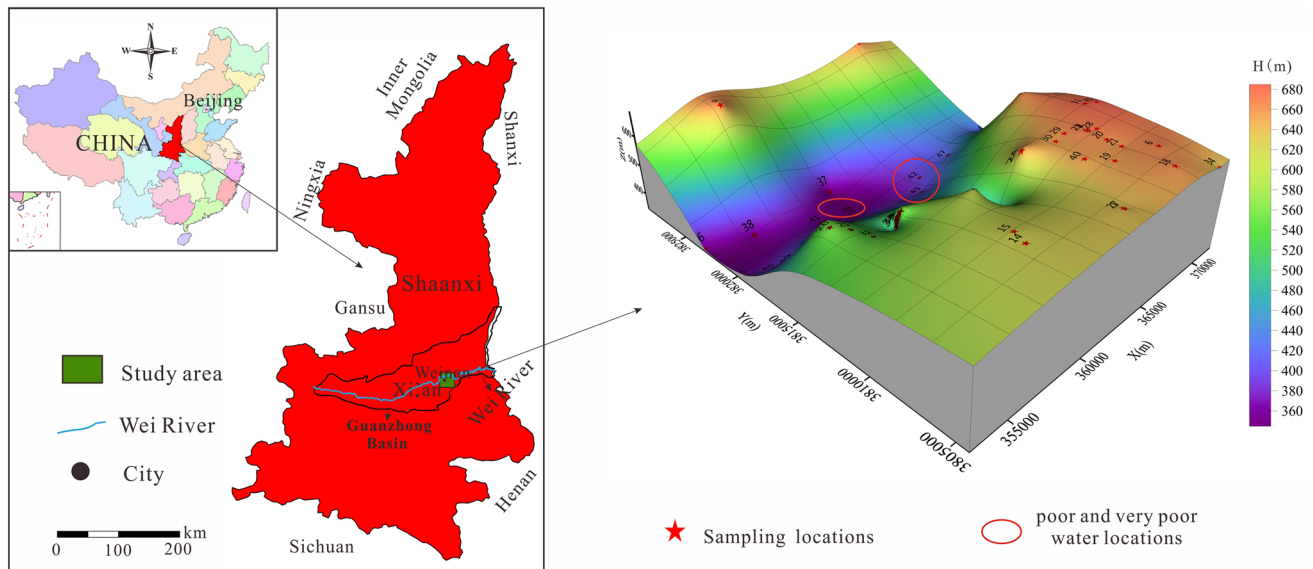


Fig. 1 Location map of groundwater samples in part of Guanzhong Basin, China

stored at 4 °C until analysis. Figure 1 shows the groundwater sampling points in the study region. Groundwater quality parameters, including pH, total dissolved solids (TDS), major ions (sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), chloride (Cl^-), sulfate (SO_4^{2-}), heavy metals [manganese (Mn) and Hexavalent chromium (Cr^{6+})], and other ions [ammonia nitrogen (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), and fluoride (F^-)], were analyzed for all groundwater samples. pH was measured immediately in the field using portable devices on site. TDS was determined by drying the samples at 105 °C and weighing them with an analytical balance. Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NH_4^+ , NO_3^- , NO_2^- , and F^- were tested using ion chromatograph (ICS-600). HCO_3^- and CO_3^{2-} were determined by alkalinity titration. Mn and Cr^{6+} were measured using plasma emission spectrometry (ICAP6300).

The analytical accuracy was cross-checked by calculating ionic balance error (IBE) as follows:

$$\text{IBE} = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \times 100\% \quad (1)$$

where all cations and anions were expressed in meq/L. The computed IBE was within the acceptable limit of $\pm 5\%$. In this study, the calculated results showed that the IBE ranged from -4.13 to 4.47 , which confirms the reliability of the ion analysis results.

Methods

Improved Water Quality Index (WQI)

Water quality index (WQI) is frequently used to determine the suitability of the groundwater for drinking purposes throughout the world and is an effective tool for appraising the groundwater quality (Li et al. 2010; Adimalla et al. 2018; Adimalla and Qian 2019b; Iticescu et al. 2019). When calculating WQI, the first step is to calculate the weights of the parameters. Criteria Importance Through Inter-criteria Correlation (CRITIC), proposed by Diakoulaki, is an objective weighting method, which is mainly composed of two parts (Wang et al. 2018). These two parts are represented by the following equations:

$$C_j = \delta_j \sum_{j=1}^m (1 - r_{ij}) \quad (2)$$

$$W_j = C_j / \sum_{j=1}^m C_j \quad (3)$$

where C_j represents the information amount of the j th parameter. δ_j indicates the standard deviation of the j th parameter. m is the number of different parameters. r_{ij} is the correlation coefficient. W_j is the weight of the j th parameter.

In order to eliminate the unit influence between different parameters, the data need to be normalized before calculating the weight. Let y_{ij} represent the normalized value, the correlation coefficient is calculated using the formula (4).

$$r_{ij} = \frac{\sum (x_{ij} - \bar{x}_{ij})(y_{ij} - \bar{y}_{ij})}{\sqrt{\sum (x_{ij} - \bar{x}_{ij})^2 \sum (y_{ij} - \bar{y}_{ij})^2}} \quad (4)$$

where x_{ij} is the j th evaluation index of the i th groundwater sample. \bar{x}_{ij} and \bar{y}_{ij} express the average value of x_{ij} and y_{ij} , respectively.

The second step is to assign a quality rating scale (Q_j) for each parameter. Q_j is calculated by the following formula:

$$Q_j = \frac{C_j - C_{jp}}{S_j - C_{jp}} \times 100\% \quad (5)$$

where C_j is the concentration of each chemical parameter in water sample in mg/L. C_{jp} is the ideal value of the parameter in pure water (consider $C_{jp} = 0$ for all, except pH where $C_{jp} = 7$). S_j is the standard value for each chemical parameter in mg/L according to Chinese Quality Standard for Groundwater.

Lastly, the WQI can be calculated by the formula below:

$$WQI = \sum_{j=1}^m W_j Q_j \quad (6)$$

Computed WQI values were classified into five categories, excellent, good, moderate, poor, and very poor (Li et al. 2010; Adimalla et al. 2018; Zotou et al. 2019). The WQI range and type of water are shown in Table 1.

Human Health Risk Assessment (HHRA) Model

The human health risk assessment (HHRA) model established by the United States Environmental Protection Agency (USEPA) is a widely used method to evaluate the potentially harmful effects of groundwater contaminants on the health of children and adults (Li et al. 2016c, 2019b; Adimalla et al. 2019; Adimalla and Qian 2019a; Adimalla and Wu 2019). Based on the Ministry of Environmental Protection (MEP) of the P.R. China, there are two main

channels through which are human body absorbs harmful substances from groundwater, they are orally drinking water and dermal contact (Li et al. 2016c; Wu and Sun 2016; Adimalla and Qian 2019a). The HHRA includes non-carcinogenic risks and carcinogenic risks. The non-carcinogenic risks were assessed using NH_4^+ , NO_3^- , NO_2^- , Mn^{2+} , F^- , and Cr^{6+} as the risk assessment parameters. The models for non-carcinogenic risks via ingestion and dermal contact are as follows (Li et al. 2016c; Wu and Sun 2016; Adimalla et al. 2019).

$$\text{CDI} = \frac{C \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (7)$$

$$\text{HQ}_{\text{oral}} = \frac{\text{CDI}}{\text{RfD}_{\text{oral}}} \quad (8)$$

The non-carcinogenic risk through dermal contact is expressed as (Li et al. 2017b):

$$\text{CDD} = \frac{\text{DA} \times \text{EV} \times \text{SA} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (9)$$

$$\text{DA} = K \times C \times t \times \text{CF} \quad (10)$$

$$\text{SA} = 239 \times H^{0.417} \times \text{BW}^{0.517} \quad (11)$$

$$\text{HQ}_{\text{dermal}} = \frac{\text{CDD}}{\text{RfD}_{\text{dermal}}} \quad (12)$$

$$\text{RfD}_{\text{dermal}} = \text{RfD}_{\text{oral}} \times \text{ABS}_{\text{gi}} \quad (13)$$

Therefore, the total non-carcinogenic risks are calculated as follows:

$$\text{HI}_j = \text{HQ}_{\text{oral}} + \text{HQ}_{\text{dermal}} \quad (14)$$

$$\text{HI}_{\text{total}} = \sum_{j=1}^m \text{HI}_j \quad (15)$$

where CDI: chronic daily dose via ingestion (mg/kg day), C : concentration of pollutant for groundwater (mg/L), HQ_{oral} and $\text{HQ}_{\text{dermal}}$: hazard quotient through oral and dermal exposure pathways, CDD: chronic daily dose via dermal contact (mg/kg day), DA: exposure dosage (mg/cm²), SA: skin surface area (cm²), RfD_{oral} and $\text{RfD}_{\text{dermal}}$: reference dosage via oral and dermal contact (mg/kg day), and ABS_{gi} : gastrointestinal absorption factor. The meanings and index values of other parameters are shown in Tables 2 and 3.

In addition to the non-carcinogenic risk, Cr^{6+} can also create carcinogenic risks for humans (Li et al. 2016c). The carcinogenic risks of Cr^{6+} through drinking water intake and dermal contact are calculated as follows:

Table 1 Classification of groundwater based on TDS

WQI	Rank	Water quality
< 50	1	Excellent
50–100	2	Good
100–150	3	Medium
150–200	4	Poor
> 200	5	Extremely poor

$$CR_{\text{oral}} = CDI \times SF_{\text{oral}} \quad (16)$$

risk assessments is set at 25,550 days for both adults and children. The acceptable limit for CR is 1×10^{-6} .

$$CR_{\text{dermal}} = CDD \times SF_{\text{dermal}} \quad (17)$$

$$SF_{\text{dermal}} = \frac{SF_{\text{oral}}}{ABS_{\text{gi}}} \quad (18)$$

$$CR_{\text{total}} = CR_{\text{oral}} + CR_{\text{dermal}} \quad (19)$$

where CR denotes the carcinogenic risk. SF is the slope factor for the carcinogenic contaminants $(\text{mg}/\text{kg day})^{-1}$. The SF_{oral} value for Cr^{6+} was set at $0.42 (\text{mg}/\text{kg day})^{-1}$ according to the Chinese technical guidelines for risk assessments of contaminated sites (Ministry of Health of the P.R. China, S. A. o. t. P. R. C. 2006). The $EF \times ED$ of CDI for carcinogenic

Results and Discussion

Groundwater Chemistry

Physiochemical Parameters

The statistical results of water quality for the 51 groundwater samples are illustrated in Table 4. Table 4 also shows the details of drinking water quality limits. The pH values of the groundwater are in the range of 7.1–8.4 (mean = 7.67), which does not exceed the limits of pH (6.5–8.5) and reveals that the groundwater in this area is alkaline. TDS values

Table 2 Key parameters for computing the health risks through ingestion and dermal pathways

Parameters	Males	Females	Children	Units	Parameters	Males	Females	Children	Units
Ingestion rate (IR)	1.5	1.5	0.7	L/d	Skin permeability coefficient (K)	0.001			cm/h
Exposure frequency (EF)	365	365	365	d	Contact duration (t)	0.4			h/d
Exposure duration (ED)	30	30	12	a	Conversion factor (CF)	0.001			–
Average body weight (BW)	70	55	15	kg	Average height (H)	165.3	153.4	99.4	cm
Average time (AT)	10,950	10,950	4380	d	Exposure frequency (EV)	1			d

Table 3 The values of RfD_{oral} , RfD_{dermal} , and ABS_{gi} for different ions

Parameters	RfD_{oral}	RfD_{dermal}	ABS_{gi}	Parameters	RfD_{oral}	RfD_{dermal}	ABS_{gi}
NH_4^+	0.97	0.97	1	F^-	0.04	0.04	1
NO_3^-	1.6	1.6	1	Mn^{2+}	0.14	0.14	1
NO_2^-	0.1	0.1	1	Cr^{6+}	0.003	7.5E-05	0.025

Table 4 Statistical summary of chemical composition of groundwater in the study region

Parameters	Units	Chinese Standards	Min	Max	Mean	SD	P (%)
PH	–	$6.5 \leq \text{PH} \leq 8.5$	7.1	8.4	7.67	0.370	100
TDS	mg/L	≤ 1000	497.26	2198.82	734.64	306.475	90.2
$\text{K}^+ + \text{Na}^+$	mg/L	≤ 200	6.67	315.33	91.35	69.257	92.2
Ca^{2+}	mg/L	≤ 200 (WHO 2008)	9.22	265.53	55.78	36.917	98
Mg^{2+}	mg/L	≤ 150 (WHO 2008)	3.65	190.91	37.62	27.050	98
HCO_3^-	mg/L	–	300.81	1020.22	418.17	112.833	–
SO_4^{2-}	mg/L	≤ 250	0	903.02	79.32	133.882	94.1
Cl^-	mg/L	≤ 250	5.32	242.9	35.38	46.586	100
CO_3^{2-}	mg/L	–	0	12	4.28	4.116	–
NH_4^+	mg/L	≤ 0.20	0	0.14	0.048	0.057	100
NO_3^-	mg/L	≤ 20.0	0	36	16.3	17.530	94.1
NO_2^-	mg/L	≤ 0.02	0	180	16.98	35.926	62.7
F^-	mg/L	≤ 1.0	0	13.2	1.89	2.797	88.2
Mn^{2+}	mg/L	≤ 0.10	0	0.36	0.05	0.065	96.1
Cr^{6+}	mg/L	≤ 0.05	0	0.012	0.008	0.001	100

P percentage of the sample below the permissible limits

varied in a wide range of 497.26–2198.82 mg/L, with a mean value of 734.64 mg/L. According to the standard limits of TDS (< 1000 mg/L), 9.8% groundwater samples show unhealthy and unpalatable for human health.

The ionic dominance pattern was in the order of $K^+ + Na^+ > Ca^{2+} > Mg^{2+} > NH_4^+$ for cations and $HCO_3^- > SO_4^{2-} > Cl^- > NO_2^- > NO_3^- > CO_3^{2-} > F^-$ for anions. The average concentrations of $K^+ + Na^+$, Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , NH_4^+ , NO_3^- , NO_2^- , and F^- in groundwater were 91.35, 55.78, 37.62, 35.38, 79.32, 418.17, 4.28, 0.048, 16.3, 16.98, and 1.89 mg/L (Table 4). Concentrations of sodium and bicarbonate were the highest among the cations and anions, respectively. A certain amount of sodium is very essential to maintain a human health, whereas excess sodium intake will cause adverse health risks such as hypertension and osteoporosis (Adimalla and Qian 2019a; Li et al. 2019a). According to Drinking Water Quality Standard of P.R. China (Ministry of Health of the P.R. China 2006), the percentage of $K^+ + Na^+$ below the permissible limits is 92.2. Ca^{2+} and Mg^{2+} are also essential to human health. When the human body lacks Ca^{2+} , it leads to several diseases such as stroke, osteoporosis, and colorectal cancer. High Mg^{2+} concentration acts as a laxative agent (WHO 2011; Adimalla and Qian 2019a). In the present study, 98% of the groundwater sampling locations were within the maximum allowable limit for Ca^{2+} and Mg^{2+} (Table 4). In addition, the concentrations of HCO_3^- and CO_3^{2-} ranged from 300.81 to 1020.22 mg/L and 0 to 12 mg/L, respectively. The SO_4^{2-} concentration of groundwater in study area varied from 0 to 903.02 mg/L. 94.1% of the groundwater samples were within the desirable limit of 250 mg/L for SO_4^{2-} in the study region. Chloride concentration ranged from 5.32 to 242.9 mg/L and all groundwater samples were within the upper limit (≤ 250 mg/L) for drinking water.

The study area is an agricultural region with wide fertilizer and pesticide use (Quan 2018; <https://www.sxxx.gov.cn/zxhy/ydxszth/15351.html>). Therefore, the study assessed the presence of nitrogen pollution. The NH_4^+ concentration of all groundwater samples was within the desirable limit for drinking (Table 4). However, the concentration of NO_3^- and NO_2^- for all groundwater samples in study region varied from 0 to 36 mg/L and 0 to 180 mg/L, respectively. 94.1% and 62.7% of groundwater samples were within the upper limit of 20 and 0.02 mg/L for NO_3^- and NO_2^- in the study region. Despite high levels of nitrite ions at two sampling points (44 and 47) in the study area, no reports of blue infant disease have been heard. Moreover, fluoride (F^-) is a necessary element for human health at low concentration, but has non-carcinogenic risks at a high level, causing endemic fluorosis (dental and skeletal) and damage to the soft tissues (liver, kidney, lung, testis, etc.) (Duan et al. 2018; Ganyaglo et al. 2019). In this study, the F^- concentration ranged from 0

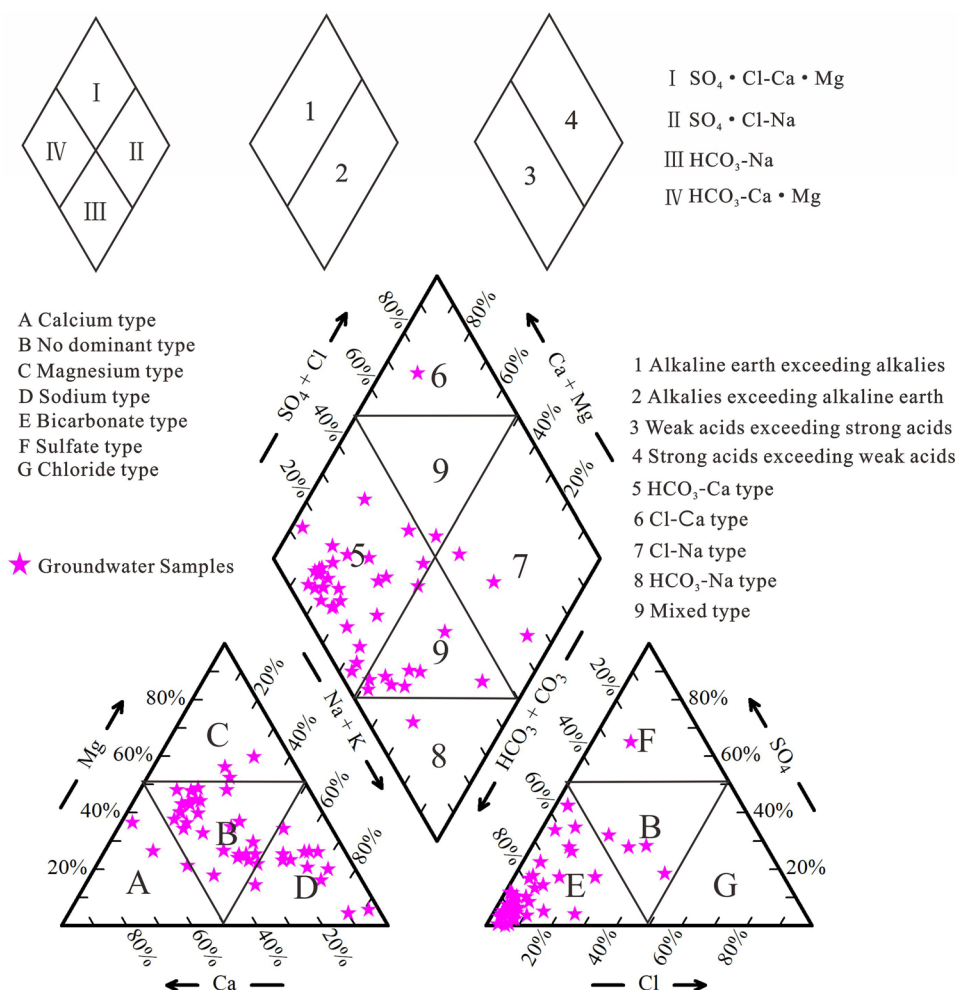
to 13.2 mg/L. Six groundwater samples were not suitable for drinking, based on this parameter with 11.8% of all samples exceeding the upper limit (≤ 1.0 mg/L). High fluoride content in the study area leads to high incidence of dental and skeletal fluorosis (Li et al. 2009; Liu 2009). Therefore, the pollution from nitrogen (NO_2^- and NO_3^-) and fluoride was the most serious in the study region. In addition, the Mn^{2+} concentrations for all samples ranged from 0 to 0.36 mg/L, with a mean of 0.05 mg/L (Table 4). In the study region, 96.1% of groundwater samples were within the upper limit of 0.1 mg/L for Mn^{2+} . The Cr^{6+} concentration of all groundwater samples was within the desirable limit for drinking.

The Dominant Water Types

Hydrochemical types are governed by major ions and are usually classified by a piper diagram (Piper 1944; He and Li 2019; Li et al. 2016c; Xu et al. 2019a). As shown in Fig. 2, cations of groundwater samples in the study region were mainly plotted in zones B and D, indicating that groundwater in the study area is mainly of the “no dominant” type and the “sodium” type. Anions were mainly plotted in zone E, followed by B, indicating that the groundwater is mainly of the “bicarbonate” type and “no dominant” type. Almost all groundwater samples were plotted in zones III and IV, followed by zone II, illustrating that HCO_3^-Na and $HCO_3^-Ca \cdot Mg$ were the dominant water types, followed by the $SO_4 \cdot Cl-Na$ type. The hydrochemical types are mainly related to the carbonate-rich material dissolution within the aquifers (Xu et al. 2019a).

Groundwater Chemistry Formation

The Gibbs diagrams are helpful to analyze the relationship between water chemistry and aquifer lithology (Gibbs 1970; He and Li 2019; Li et al. 2016c; Adimalla and Qian 2019b; Chen et al. 2019; Xu et al. 2019a). There are three main natural mechanisms forming the water chemistry in these diagrams: evaporation dominance, rock dominance, and precipitation dominance (Fig. 3). As shown in Fig. 3, the groundwater samples of “bicarbonate type” were mainly in the zone of rock dominance, which suggested that rock weathering and leaching are the major mechanisms controlling groundwater chemistry in these areas. However, the distributions of “no dominant type” and “chloride type” showed a slightly increasing trend toward the evaporation-dominant zone. This is related to the local semi-arid climate with little rainfall and large evaporation. Therefore, the main mechanisms governing groundwater chemistry of “chloride type” in this area are rock weathering and evaporation.

Fig. 2 Piper diagram of groundwater samples

Groundwater Quality for Drinking

Groundwater samples ($n=51$) and its WQI values and ranks are presented in Table 5. The results of WQI ranged from 21.02 to 966.98. Out of 51 groundwater samples, water quality of 1 and 2 samples was categorized as poor and extremely poor, and 48 samples were suitable for drinking purposes (rank = 1, 2, 3) (Table 5). The assessment results indicated that the samples suitable for drinking water account for 94.12% of the total samples, while the samples unsuitable for drinking account for 5.88%.

Spatial distribution of WQI is also shown in Fig. 4. It can be seen from Fig. 4 that the poor and extremely poor water samples are mainly located in the Weihe Plain in the central and northern parts of study area. It implies that human activities, including extensive use of fertilizers, septic tank leakage, and effluent of organic matter, are considered to have a greater impact on the groundwater quality of the study area. In addition, the lower the elevation, the worse is the groundwater quality in the study region (Figs. 1 and 4). This phenomenon indicated that groundwater will be affected by

the geological environment and human factors during the flow process, and the flow of groundwater is basically the same as that of surface water in the study region, flowing from a high elevation to a low elevation.

Human Health Risk Assessment

The health risk assessment (HRA) model is the most effective tool for calculating the non-carcinogenic health risk in the different age groups (Li et al. 2016c, 2019b; Adimalla and Qian 2019a, b). The calculated results of non-carcinogenic health risks for adults and children in the study region through oral intake and dermal contact are explicitly presented in Table 5. As shown in Table 5, the HQ_{oral} values ranged from 0.0002 to 38.5714, with a mean of 2.6540 for males in the study region. The HQ_{oral} values for females ranged from 0.0002 to 49.0909, with a mean of 3.3778. And the HQ_{oral} values for children varied from 0.0003 to 84.0000, with a mean of 5.7797. The results of the $\text{HQ}_{\text{dermal}}$ values were smaller than HQ_{oral} , ranging from 7.38×10^{-7} to 1.86×10^{-1} for males, 8.04×10^{-7} to 2.03×10^{-1} for females,

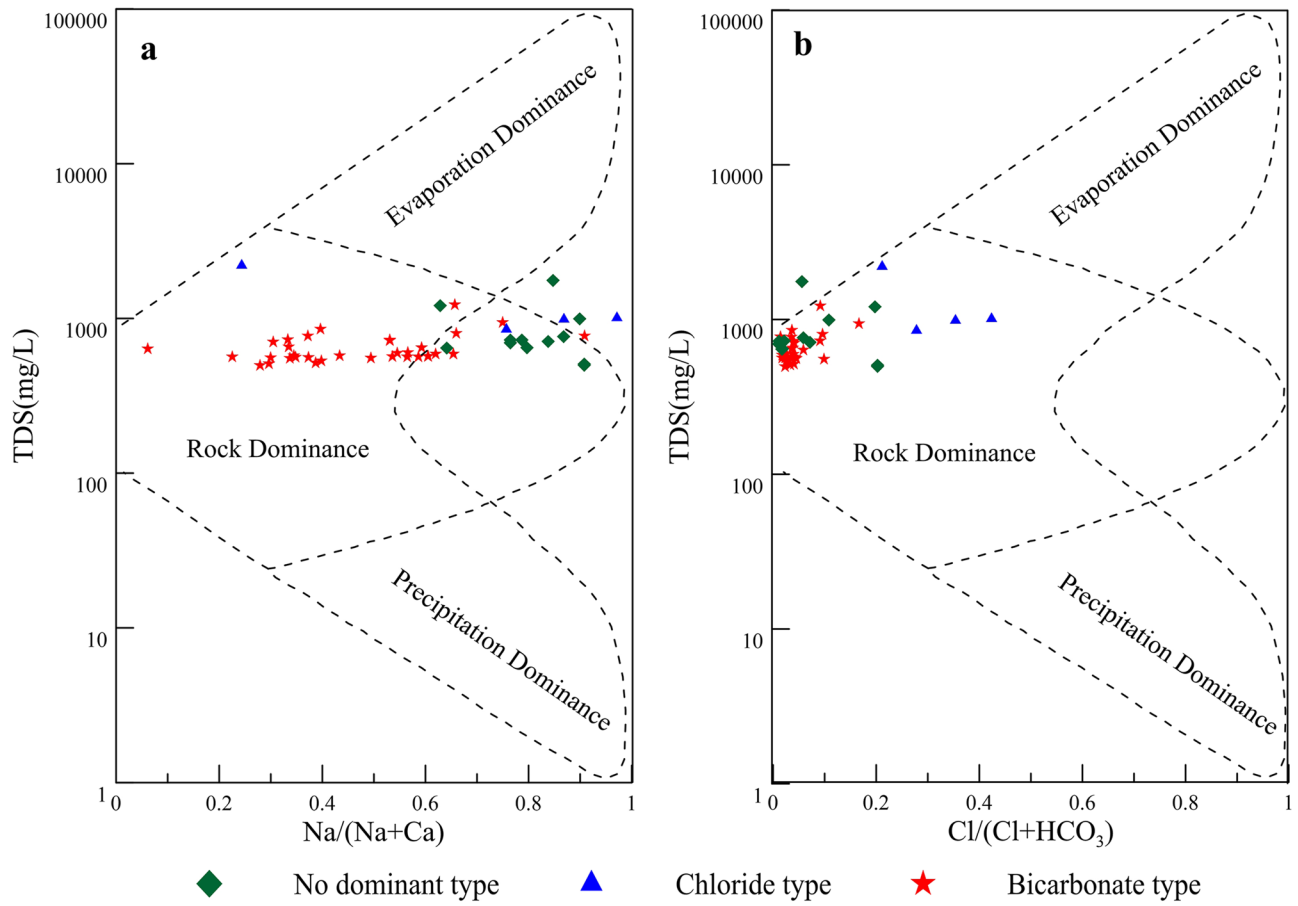


Fig. 3 Gibbs diagrams of groundwater samples **a** TDS vs. $Na/(Na+Ca)$; **b** TDS vs. $Cl/(Cl+HCO_3)$

Table 5 Assessment results according to computed WQI

Numbers	WQI	Rank	Numbers	WQI	Rank	Numbers	WQI	Rank
1	28.24	1	18	26.47	1	35	41.78	1
2	36.45	1	19	47.80	1	36	74.32	2
3	54.34	2	20	24.85	1	37	62.45	2
4	37.79	1	21	31.35	1	38	83.72	2
5	30.61	1	22	31.86	1	39	65.50	2
6	25.18	1	23	44.73	1	40	30.95	1
7	31.32	1	24	22.25	1	41	60.52	2
8	44.80	1	25	28.11	1	42	42.69	1
9	40.03	1	26	26.78	1	43	28.74	1
10	33.65	1	27	29.29	1	44	966.98	5
11	21.02	1	28	25.97	1	45	41.07	1
12	28.38	1	29	25.35	1	46	129.54	3
13	24.14	1	30	41.88	1	47	858.72	5
14	23.44	1	31	37.60	1	48	193.22	4
15	24.08	1	32	70.17	2	49	67.45	2
16	27.82	1	33	62.25	2	50	31.89	1
17	28.61	1	34	92.14	2	51	32.41	1

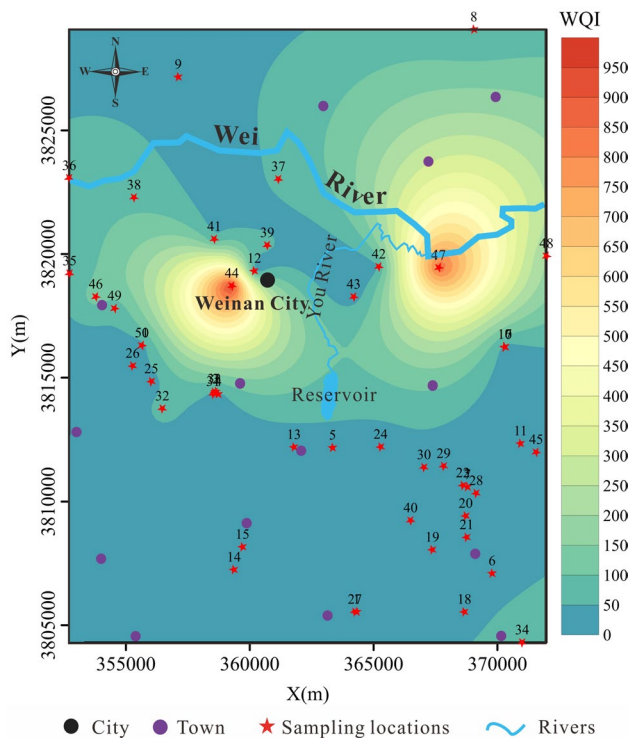


Fig. 4 Zoning map of different water quality

and 1.26×10^{-6} to 3.17×10^{-1} for children, with means of 1.27×10^{-2} , 1.38×10^{-2} , and 2.16×10^{-2} , respectively. This suggests that for non-carcinogenic risk, dermal contact pathway is quite low as compared with the ingestion pathway. The results of the HQ_{total} values ranged from 0.0002 to 38.7575 for males and from 0.0002 to 49.2935 for females, with means of 2.6666 and 3.3916, respectively. For children, the HQ_{total} values varied from 0.0003 to 84.3167, with a mean of 5.8013 (Table 6). 23.53%, 25.49%, and 37.25% of the samples have HQ_{total} exceeding 1, suggesting that most samples may induce non-carcinogenic risk to males, females, and children, respectively. These results showed the health risk of children and females is much higher than males. The reason is that children are more vulnerable is that they have smaller body weights than that of adult females and males (Li et al. 2016c).

As discussed earlier, non-carcinogenic risks are high in study region for adults and children. Table 7 shows the interval values for non-carcinogenic risks of different ions in drinking water. As shown in Table 7, the non-carcinogenic risk for adults and children was generally observed in the order of $NO_2^- > F^- > NO_3^- > Cr^{6+} > Mn^{2+} > NH_4^+$. The pattern also indicated that the pollution from nitrogen (NO_2^- and NO_3^-) and fluoride was the most serious in the study region. The extensive use of fertilizers in agricultural applications is typically the cause for the high nitrogen concentration in groundwater of the study region. Also, nitrogen

contamination can potentially originate from septic tank leakage and effluent organic matter (Kihumba et al. 2016; Adimalla et al. 2019). This is a serious issues because high nitrogen concentration could cause debilitating health disorders, such as gastric cancer, goiters, methemoglobinemia, birth defects, and hypertension (Zhang et al. 2018; Adimalla and Wu 2019; He et al. 2019). In addition to nitrogen, fluorine is another concern and widely distributed in the Earth's crust and exists in a number of fluoride rich minerals, such as fluorite (CaF_2), fluorapatite ($Ca_5(PO_4)_3F$), villiumite (NaF), and topaz ($Al_2(SiO_4)F_2$), and so on (Adimalla et al. 2019; Adimalla and Wu 2019). Alkaline conditions favor the dissolution of fluoride minerals (Jia et al. 2019). Also, industrial sources, such as coal combustion, brick kilns, aluminum smelting, glass, and coal-based power stations, also can release fluoride into the environment, depositing and entering the water. Therefore, there is also a high fluorine concentration in the study region. The higher the concentration of hazardous substances in drinking water is, the greater the risk of disease on human health is.

The HQ_{total} limits for non-carcinogenic risk for human health should not exceed 1, so the existence of Cr^{6+} would merely cause non-carcinogenic risk to children, but no non-carcinogenic risk to adult males and females in the study region. As an aside, the presence of Mn^{2+} in the study area does not cause non-carcinogenic risks for adults and children.

Additionally, the results of carcinogenic health risk for Cr^{6+} are shown in the Fig. 5. It can be seen from Fig. 5 that the carcinogenic health risks for adult male, adult female, and children mainly occur in the south of the study region, especially in the mountains in the southeast. Since there is no large industrial distribution in this area, the reason for the high Cr^{6+} content in the southeast in the study region may be related to the geological environment of the area. Gu et al. (2015) conducted the similar research. Furthermore, the health risk of children is also much higher than males and females, and the distribution area of carcinogenic health risk for children is wider than females and males. It can be seen that although the content of Cr^{6+} does not exceed the limit (0.05 mg/L) of drinking water, there is also a great carcinogenesis risk for different people groups.

Sustainable Groundwater Quality Management and Possible Options

Groundwater is critical for the life of humans, animals, and plants, especially in areas where surface water is scarce. However, groundwater pollution is getting worse in areas where water treatment procedures are absent (Jia et al. 2019). The results of this study have indicated that the groundwater in the study region that is available for consumption is not totally healthy for humans. Therefore,

Table 6 The non-carcinogenic risks results of HHRA through drinking water intake and dermal contact

Samples	HQ _{oral}			HQ _{dermal}			HQ _{total}		
	Male	Females	Children	Male	Females	Children	Male	Females	Children
1	0.1755	0.2234	0.3822	8.46E-04	9.22E-04	1.44E-03	0.1764	0.2243	0.3837
2	0.0991	0.1262	0.2159	4.78E-04	5.21E-04	8.14E-04	0.0996	0.1267	0.2167
3	0.1512	0.1924	0.3292	7.29E-04	7.94E-04	1.24E-03	0.1519	0.1932	0.3304
4	0.0894	0.1138	0.1946	4.31E-04	4.69E-04	7.34E-04	0.0898	0.1142	0.1954
5	0.0081	0.0103	0.0177	3.91E-05	4.26E-05	6.65E-05	0.0081	0.0104	0.0177
6	0.2061	0.2623	0.4488	9.94E-04	1.08E-03	1.69E-03	0.2071	0.2634	0.4505
7	0.1397	0.1778	0.3043	6.74E-04	7.34E-04	1.15E-03	0.1404	0.1786	0.3054
8	0.1323	0.1684	0.2881	6.38E-04	6.95E-04	1.09E-03	0.1329	0.1691	0.2892
9	7.3442	9.3471	15.9940	3.53E-02	3.85E-02	6.02E-02	7.3795	9.3856	16.0542
10	7.2953	9.2849	15.8875	3.51E-02	3.82E-02	5.98E-02	7.3304	9.3231	15.9472
12	0.1452	0.1847	0.3161	6.25E-04	6.80E-04	1.06E-03	0.1458	0.1854	0.3172
13	0.0296	0.0377	0.0644	6.73E-05	7.33E-05	1.15E-04	0.0297	0.0377	0.0646
14	0.1788	0.2276	0.3894	7.87E-04	8.57E-04	1.34E-03	0.1796	0.2285	0.3908
15	0.1689	0.2149	0.3678	7.39E-04	8.05E-04	1.26E-03	0.1696	0.2157	0.3690
16	0.7209	0.9175	1.5700	3.18E-03	3.46E-03	5.41E-03	0.7241	0.9210	1.5754
17	1.6738	2.1303	3.6452	4.67E-03	5.08E-03	7.94E-03	1.6785	2.1354	3.6532
18	0.1520	0.1935	0.3311	6.58E-04	7.16E-04	1.12E-03	0.1527	0.1942	0.3322
19	0.8607	1.0955	1.8744	4.08E-03	4.44E-03	6.94E-03	0.8648	1.0999	1.8814
20	0.2370	0.3016	0.5161	9.79E-04	1.07E-03	1.67E-03	0.2380	0.3027	0.5178
21	0.7735	0.9844	1.6844	3.65E-03	3.98E-03	6.22E-03	0.7771	0.9884	1.6907
22	0.4244	0.5402	0.9243	1.67E-03	1.82E-03	2.84E-03	0.4261	0.5420	0.9271
23	0.2848	0.3625	0.6203	1.24E-03	1.35E-03	2.11E-03	0.2861	0.3639	0.6224
24	0.4046	0.5149	0.8811	1.89E-03	2.06E-03	3.22E-03	0.4065	0.5170	0.8843
25	0.2622	0.3338	0.5711	9.93E-04	1.08E-03	1.69E-03	0.2632	0.3348	0.5728
26	1.1316	1.4403	2.4644	5.23E-03	5.70E-03	8.91E-03	1.1369	1.4460	2.4734
27	0.2639	0.3358	0.5746	1.27E-03	1.39E-03	2.17E-03	0.2651	0.3372	0.5768
28	0.5816	0.7403	1.2667	2.29E-03	2.50E-03	3.90E-03	0.5839	0.7428	1.2706
29	0.1210	0.1540	0.2634	5.83E-04	6.35E-04	9.93E-04	0.1216	0.1546	0.2644
30	1.2054	1.5341	2.6250	5.81E-03	6.33E-03	9.90E-03	1.2112	1.5404	2.6349
31	0.0930	0.1184	0.2026	4.49E-04	4.89E-04	7.64E-04	0.0935	0.1189	0.2034
32	2.7352	3.4812	5.9567	1.32E-02	1.44E-02	2.25E-02	2.7484	3.4955	5.9791
33	1.7173	2.1857	3.7400	8.28E-03	9.02E-03	1.41E-02	1.7256	2.1947	3.7541
34	3.6980	4.7065	8.0533	1.78E-02	1.94E-02	3.04E-02	3.7158	4.7259	8.0837
35	0.0002	0.0002	0.0003	7.38E-07	8.04E-07	1.26E-06	0.0002	0.0002	0.0003
36	0.0031	0.0039	0.0067	1.48E-05	1.61E-05	2.51E-05	0.0031	0.0039	0.0067
37	0.7500	0.9545	1.6333	3.62E-03	3.94E-03	6.16E-03	0.7536	0.9585	1.6395
38	0.4316	0.5494	0.9400	2.08E-03	2.27E-03	3.54E-03	0.4337	0.5516	0.9435
40	0.0050	0.0064	0.0109	2.42E-05	2.63E-05	4.12E-05	0.0050	0.0064	0.0110
42	0.4836	0.6156	1.0533	2.33E-03	2.54E-03	3.97E-03	0.4860	0.6181	1.0573
44	38.5714	49.0909	84.0000	1.86E-01	2.03E-01	3.17E-01	38.7575	49.2935	84.3167
46	4.2857	5.4545	9.3333	2.07E-02	2.25E-02	3.52E-02	4.3064	5.4771	9.3685
47	38.5714	49.0909	84.0000	1.86E-01	2.03E-01	3.17E-01	38.7575	49.2935	84.3167
48	4.8214	6.1364	10.5000	2.33E-02	2.53E-02	3.96E-02	4.8447	6.1617	10.5396
49	0.0055	0.0070	0.0120	2.65E-05	2.89E-05	4.52E-05	0.0055	0.0070	0.0120
50	0.4611	0.5869	1.0042	2.16E-03	2.36E-03	3.68E-03	0.4633	0.5892	1.0079
51	0.1875	0.2386	0.4083	9.04E-04	9.85E-04	1.54E-03	0.1884	0.2396	0.4099
Mean	2.6540	3.3778	5.7797	1.27E-02	1.38E-02	2.16E-02	2.6666	3.3916	5.8013

Due to the data absence of the 11th, 39th, 41th, 43th, and 45th samples, the results of these points are not in Table 6

Table 7 Interval values of non-carcinogenic risks of contaminants in drinking water

Risk	Males	Females	Children
NH ₄ ⁺	[0.00022, 0.00666]	[0.00028, 0.00847]	[0.00048, 0.01449]
NO ₃ ⁻	[0.00027, 1.21117]	[0.00034, 1.54042]	[0.00059, 2.63490]
NO ₂ ⁻	[0.00129, 38.7575]	[0.00164, 49.2935]	[0.00281, 84.3167]
Mn ²⁺	[0.00015, 0.05537]	[0.00020, 0.07042]	[0.00033, 0.12045]
F ⁻	[0.11304, 7.10553]	[0.14377, 9.03714]	[0.24592, 15.4581]
Cr ⁶⁺	[0.01429, 0.62894]	[0.01819, 0.80040]	[0.03113, 1.36951]

some possible strategies are recommended to enhance the sustainable groundwater quality management in the study area.

- In consideration of saving financial, material, and time costs, it is advisable to avoid exploiting high-fluorine and high-nitrogen water sources as much as possible. However, in the long run, the treatment measures, such as distillation and fluoride removal techniques, are necessary.
- In order to raise residents' awareness of protecting the water sources, education on water conservation should be carried out. Governments and non-governmental organizations should also take measures to optimize the monitoring network and enhancing cooperation and data sharing to improve the groundwater quality.
- Experts and scholars who study water resources should also increase their research on water quantity and quality to provide certain help for government decision-making and achieve sustainable development of the earth's water resources.

Conclusions

In this study, 51 groundwater samples were collected and analyzed for various physicochemical parameters to assess the quality using WQI and its health risk using HHRA model. The major conclusions of the study are as follows:

- (1) The groundwater is slightly alkaline, and the TDS varied in a wide range of 497.26–2198.82 mg/L. The ionic dominance pattern was in the order of $K^+ + Na^+ > Ca^{2+} > Mg^{2+} > NH_4^+$ for cations and $HCO_3^- > SO_4^{2-} > Cl^- > NO_2^- > NO_3^- > CO_3^{2-} > F^-$ for anions, respectively. HCO_3^-Na and $HCO_3^-Ca \cdot Mg$ were the dominant water types, followed by the $SO_4 \cdot Cl-Na$. Rock weathering and leaching are major mechanisms that contribute to the “bicarbonate type” groundwater, while rock weathering and evaporation are main mechanisms that govern the “chloride type” water.
- (2) According to the water quality index (WQI), groundwater samples suitable for drinking account for 94.12% of the total, while the samples unsuitable for drinking account for 5.88%. The poor and extremely poor water for human consumption are mainly located in the center and northeast of study area.
- (3) The assessment of non-carcinogenic risk showed that the risk ranged from 0.0002 to 38.7575 for males and between 0.0002 and 49.2935 for females, with means of 2.6666 and 3.3916, respectively. Also, the risk for children was even greater, ranging from 0.0003 to 84.3167, with a mean of 5.8013. The health risk for children was approximately 2.18 times and 1.71 times higher than that for adult males and females, indicating that children are more susceptible to water contamination. The pollution from nitrogen (NO_2^- and NO_3^-) and fluo-

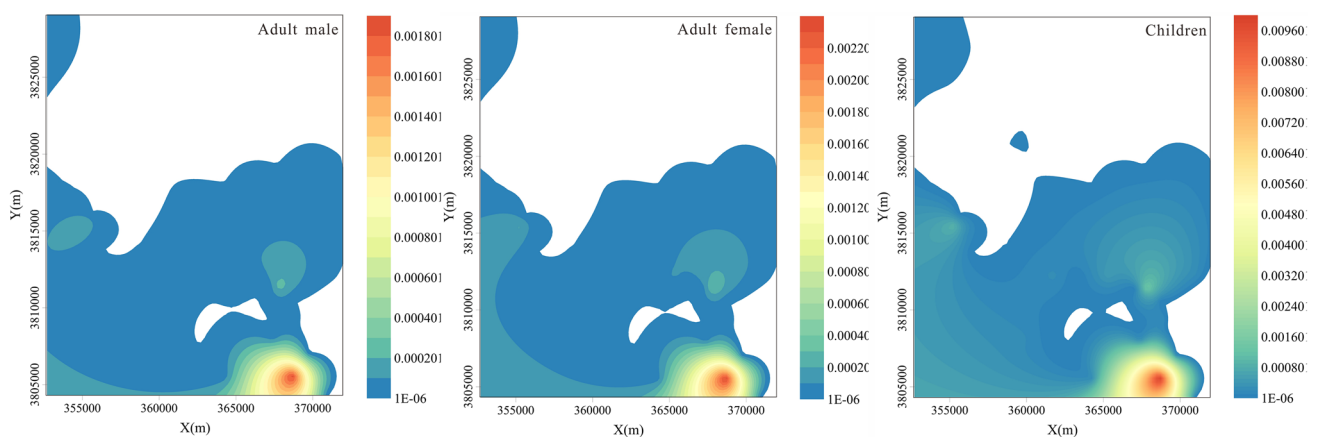


Fig. 5 Maps showing the carcinogenic health risks for adult male, adult female, and children

ride was the most serious for human health risks in the study region.

- (4) Extensive use of fertilizers, septic tank leakage, and the effluent of organic matter cause the high nitrogen concentration in groundwater for the study region. Also, the dissolution of a large amount of fluoride in the earth's crust in an alkaline environment causes high fluorine concentration of groundwater. This implies that anthropogenic activity and water rock interaction play dominant roles for the high nitrogen and fluorine concentrations. Therefore, there should be steps taken to abolish activities that contribute to this highly nitrogen- and fluorine-contaminated groundwater so the health risks can be lowered in this study region.

Acknowledgements This study was financially supported by the National Natural Science Foundation of China (Grant Nos. 41572236 and 41931285). And the completion of this article was inseparable from the contributions of all authors. Their support is gratefully acknowledged.

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