



Hydrogeochemical Characteristics, Groundwater Quality, and Health Risks from Hexavalent Chromium and Nitrate in Groundwater of Huanhe Formation in Wuqi County, Northwest China

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Abstract

This study was carried out to investigate the current status of groundwater quality in Wuqi County, northwest China. The health risk assessment was also performed to quantify the negative impacts of hexavalent chromium (Cr^{6+}) and nitrate (NO_3^-) in groundwater on human health by fully considering the gender and age of local residents. For this study, thirty groundwater samples were collected from wells and boreholes distributed in the study area and analyzed for pH, total dissolved solids (TDS), total hardness (TH), major ions ($\text{Na}^+ + \text{K}^+$, Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , and Cl^-), NO_3^- , nitrite (NO_2^-), and Cr^{6+} . Statistical analysis and graphical approaches were adopted to delineate the physicochemical parameters and hydrochemistry of groundwater. Fuzzy comprehensive method was applied in this study to appraise overall groundwater quality. The model recommended by the Ministry of Environmental Protection of the People's Republic of China was selected to assess the non-carcinogenic and carcinogenic risks caused by Cr^{6+} and NO_3^- through drinking water intake. Indicated by statistical mean values, the order of cations is $\text{Na}^+ + \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$, and that of anions is $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^-$. The averages of TH, TDS, NO_3^- , and NO_2^- are 432, 1253, 23.2, and 0.099 mg/L, respectively. Piper diagram indicates that groundwater in the study area is $\text{SO}_4\text{-Cl-Na}$ type, $\text{SO}_4\text{-Cl-Ca-Mg}$ type, and $\text{HCO}_3\text{-Na}$ type. Gibbs diagrams suggest that the major ion chemistry of groundwater in the area is governed by rock weathering and water–rock interaction, while evaporation plays a minor role. According to the results of groundwater quality assessment, over one-third (36.67%) of the groundwater samples are of poor or very poor quality. Through oral pathway, female and male adults in the study area face acceptable non-carcinogenic risks, while children face unacceptable non-carcinogenic risks caused by Cr^{6+} and NO_3^- . Both children and adults face unacceptable carcinogenic risks from Cr^{6+} . In addition, children face higher carcinogenic risks than females and males owing to smaller body weight than adults. This study may provide local authorities with insights into making scientific decisions for sustainable groundwater exploitation and efficient groundwater environmental protection.

Keywords Groundwater chemistry · Groundwater quality · Fuzzy comprehensive method · Health risks · Hexavalent chromium · Nitrate

Introduction

Groundwater is an indispensable resource for nature and social development and is used for various purposes such as domestic consumption, agricultural irrigation, industrial production, urbanization, and ecological security (Li and Qian 2018a; Li et al. 2016a; Wu and Sun 2016; Zabala et al. 2016). Especially in the arid and semiarid areas, such as the Loess Plateau in northwest China, groundwater availability is one of the key factors determining the local living standard and environmental stability (Li et al. 2016b, 2018a; Wu et al. 2015a). However, arid and semiarid areas are facing more water stresses than humid areas, not only because

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of inadequate water quantity, but also for poor water quality affected by both continuous climate change and intense human activities (Li et al. 2013, 2016c). Under this condition, studies on groundwater chemistry and groundwater pollution as well as associated health risks have drawn much attention from international scholars (Li et al. 2017a).

Considering the importance of groundwater quality in arid and semiarid regions, many studies on groundwater chemistry and quality have been carried out for guaranteeing sustainable groundwater management and protection (Li et al. 2018b; Zhang et al. 2018). Various concepts and approaches, such as statistical analysis, matter element extension analysis (MEEA), and entropy weight, have been applied to study groundwater chemistry and quality (Cai 1999; Wu et al. 2014, 2015b; Li et al. 2018c). Recently, Li et al. (2017b) combined the entropy weights and MEEA to deal with the uncertainties in groundwater quality assessment. This combination is more scientific and rational than traditional approaches in groundwater quality assessment, eliminating influences caused by some uncertain factors. Qian et al. (2013, 2014) investigated the isotopic characteristics of hydrogen and oxygen of groundwater, and determined the recharge resource of the phreatic water in Yinchuan plain, northwest China. The results are helpful in delineating the groundwater flow systems and water cycle of Yinchuan plain, and meaningful for further studies on local groundwater. Rakotondrabe et al. (2018) investigated eleven major ions and eight heavy metals in surface water and groundwater in the Mari catchment in Betare-Oya (East Cameroon) where gold mining activities were intensive, and found that the water in Mari catchment was overall acidic and not suitable for drinking. Li et al. (2016d) appraised the groundwater quality in Hua County, Shaanxi Province for drinking and irrigation purposes, and analyzed the different influencing factors of groundwater quality. The study is meaningful in preventing further groundwater pollution in Hua County, and helpful for studies in other regions facing similar problems. Busico et al. (2017) implemented three different methods, SINTACS, AVI, and LOS in Campanian Plain of southern Italy, and concluded that the combination of the three methods would generate rational results in groundwater vulnerability and pollution risk assessment.

In addition to water quality assessment, many studies also hammered at the health risks caused by contaminants in groundwater. Common contaminants in groundwater include nitrate (NO_3^-), nitrite (NO_2^-), ammonia nitrogen ($\text{NH}_4\text{-N}$), arsenic (As), fluoride (F^-), and trace metals (Li et al. 2014a, b; Zeng et al. 2018; Omid et al. 2015). Li et al. (2017c) studied the non-carcinogenic and carcinogenic risks caused by F^- , $\text{NH}_4\text{-N}$, As, phenol, hexavalent chromium (Cr^{6+}), and mercury (Hg) in Shahu Lake Tourist Area in the Ningxia Hui Autonomous Region, and concluded that As and Cr^{6+} contributed most to total health risks. One contribution of

the study is the comparison between tourists and workers based on the risks of exposure to water from three representative stations. The study pointed out the importance of taking measures to reduce arsenic and Cr^{6+} exposure, which is a scientific basis for the local decision makers to make sound decisions. Alam et al. (2016) assessed the health risks from arsenic in the Gangetic groundwater of Jharkhand in India. The study revealed the high arsenic-induced health risks to local children and adults but failed to compare the risks between different genders. Su et al. (2013) investigated the health risks from nitrate nitrogen in groundwater in an agricultural sewage irrigation area, and concluded that the health risk in agricultural areas was higher than that in urban areas. The health risk assessment successfully compared the health risks between rural areas and urban areas and between females and males with the age of local residents ranging from 1 month to 80 years.

Wuqi County is located in arid and semiarid Loess Plateau in Shaanxi Province, northwest China. Influenced by the semiarid climate and the broken loess geomorphology, groundwater in this area is scarce and distributes unevenly (Li and Qian 2018b; Tuo et al. 2016). However, it is an important source of water for multiple uses in this area. In recent years, because of the rapid development of agriculture, industry, and urbanization, the demand of water resources has increased, which negatively induces groundwater contamination (Xie et al. 2012). Understanding the current status of groundwater quality is important for the sustainable development of the county, and is also of great importance to guarantee the safety of water supply for local residents. However, there is no such a study before according to our knowledge. Therefore, the main objectives of the research are (1) to investigate the groundwater chemistry and appraise the groundwater quality through graphical approaches and fuzzy comprehensive assessment method, and (2) to assess the non-carcinogenic and carcinogenic risks from Cr^{6+} and NO_3^- in groundwater using the model recommended by the Ministry of Environmental Protection of the People's Republic of China (2014) to quantify the potential impacts of these contaminants in groundwater on human health. The study is designed for the local authorities to make considerable decisions about groundwater exploitation, management, and protection.

Study Area

Geomorphology and Climate

Wuqi County is located in the north of the Loess Plateau and is administratively governed by Yan'an City (Fig. 1). The elevation is higher in the north, northwest, and southwest, but is lower in the middle, east, and southeast, with

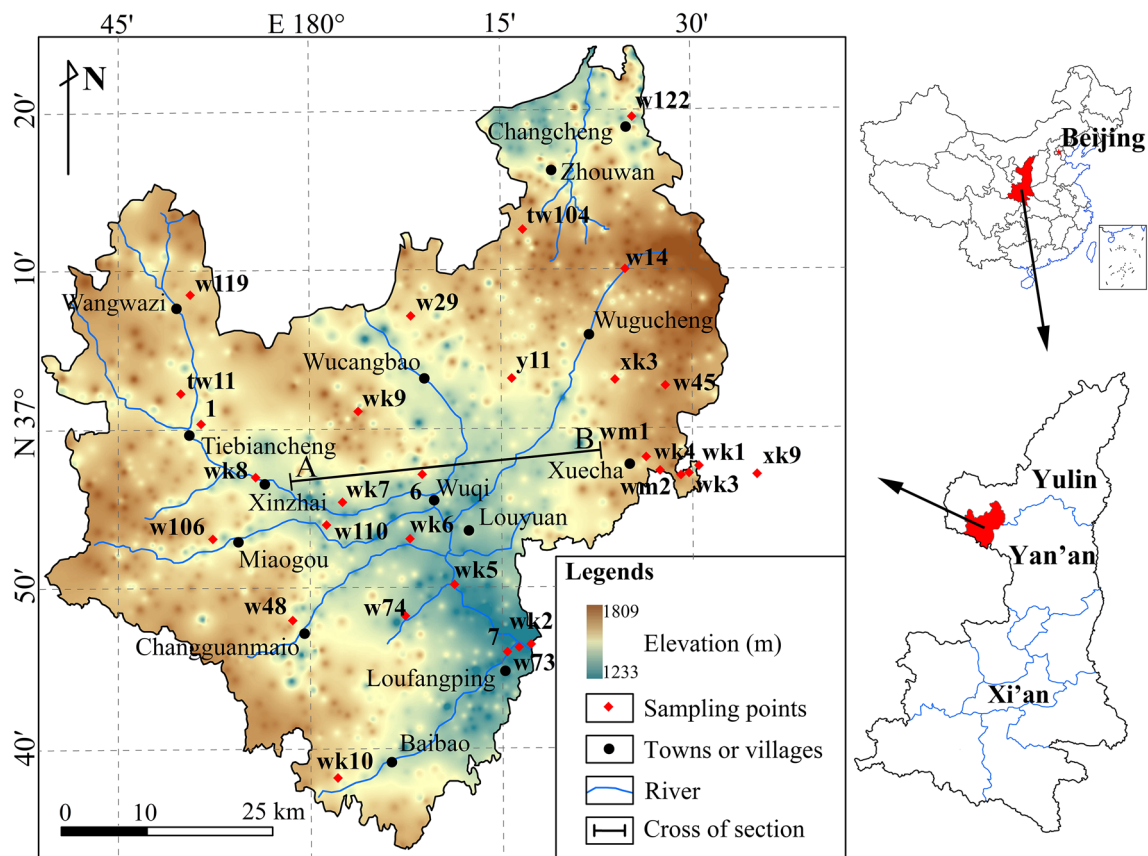


Fig. 1 Location and terrain of the study area

elevation ranging from 1233 to 1809 m above the mean sea level. The Luo River flows through the study area from the northwest to the southeast. The landforms in the study area are main loess tableland, loess hills and ridges, and small alluvial terraces. Loess gullies are widely distributed in the area, which makes the area fragmented. The terraces are mainly distributed along the main streams of the rivers, with the terrace widths ranging from 150 to 350 m and elevation ranging from 1230 to 1400 m above the mean sea level.

The study area lies within the temperate continental monsoon climate zone with rainfall occurring mainly in summer. The spring in this area is windy and cold, and sometimes dust storms may occur in spring and winter, while in autumn the climate is cool and pleasant. According to the data from local weather station, the mean annual precipitation in the study area is 443.7 mm, and rainfall mainly occurs from June to September, accounting for approximately 73% of the annual rainfall. The mean annual temperature of the study area is 8.6 °C with the highest in July and the lowest in January. The annual evaporation rate in the area is approximately 960.7 mm, which is over twice of the precipitation.

Geology and Hydrogeology

The stratum exposed in the study area mainly includes Huanhe formation (K_1h) of Mesozoic Cretaceous, the Cenozoic Neogene and the Quaternary (Fig. 2), and the groundwater in the first strata, Huanhe formation, is studied in this article. Huanhe formation is mainly outcropped at the western side along the Zhangqu–Liuping–Danba–Yizheng line, with thickness gradually increasing from east to west, ranging from 0 to 550 m. Huanhe formation can be divided into three parts. The upper section of Huanhe formation is composed of mudstone with arkosic sandstone intercalation. The middle portion is mainly composed of arkose and mudstone, with hard ferric and calcic cementation in it. The lithological component of the lower part almost covers arkose with a little sandy mudstone. The pores and fractures developed in bedrock of Huanhe formation provide the main space for groundwater occurrence and storage.

The groundwater is widely distributed in the Huanhe formation, with thickness of the aquifer ranging from 40 to 200 m, with porosity varying from 0.1 to 0.2, and fissure ratio around 0.25. The hydraulic conductivity of the aquifer is generally between 0.01 and 0.10 m per day. The

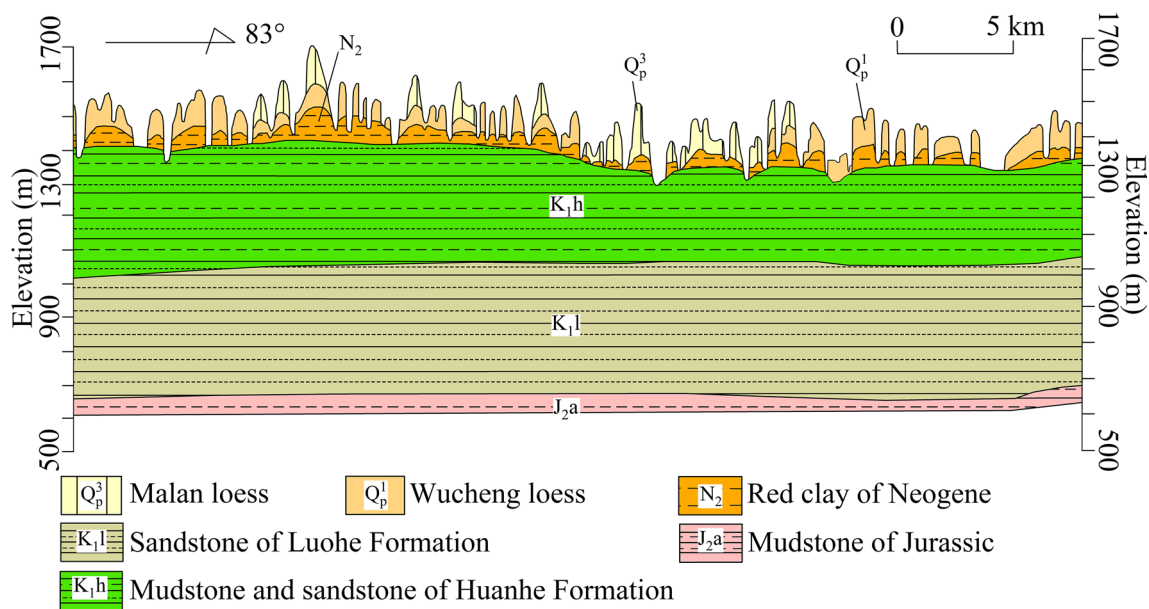


Fig. 2 Geological section from Tiebiancheng Town to Shunning Village

groundwater in Huanhe formation is confined in the west of the study area, and is unconfined in the east. The groundwater in Huanhe formation is recharged mainly from precipitation at the exposed portion of the aquifer, and the river water percolation is also a vital recharge source of the Huanhe aquifer. Controlled by the topography, groundwater in Huanhe formation flows towards the rivers and streams in the study area, and eventually drains to the Luo River and Yan River. According to the groundwater monitoring data, there are two types of groundwater dynamic regimes, including the fluctuating type and the declining type. The fluctuating type mainly occurs in the west and northeast of the study area, with the water table depth varying from 0.5 to 1.0 m. And the declining type mainly distributes in the middle and southeast of the study area, where concentrated groundwater mining occurs.

Materials and Methods

Sample Collection and Analysis

For this study, 30 groundwater samples were collected from wells and boreholes, and their locations were recorded with a portable GPS device and are shown in Fig. 1. These wells and boreholes were drilled by the local residents or authorities for drinking and irrigation purposes. Water samples were collected using centrifugal pump with pumping rates varying according to the permeability of the aquifer media. Before sampling, the stagnant water stored in the well pipes was pumped out for 10 min to minimize the influence of

residual water in the wells on the analysis results. All samples were collected using precleaned 2.5-L plastic bottles. Before sampling, all containers were washed and rinsed three times using the water to be sampled. pH was tested on site with a portable pH meter before acidification. After sampling, the samples were sealed and sent to laboratory for further physicochemical analysis. Sample collection and preservation followed the national technical regulations (Ministry of Environmental Protection of People's Republic of China 2009). Among these samples, 16 samples were analyzed for pH, major ions ($\text{Na}^+ + \text{K}^+$, Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and HCO_3^-), TDS, NO_3^- , Cr^{6+} , and TH to reveal the general groundwater chemistry and the contamination. The other 14 water samples were analyzed only for contaminants including pH, Cl^- , SO_4^{2-} , NO_3^- , Cr^{6+} , and TH to emphasize the contamination in groundwater and associated health risks to local residents. Routine titrimetric methods were used to measure Cl^- , SO_4^{2-} , and HCO_3^- ; EDTA titrimetric method was adopted to determine Ca^{2+} , Mg^{2+} , and TH; and $\text{Na}^+ + \text{K}^+$ was detected by flame atomic absorption spectrometry. TDS was measured through traditional drying and weighing approach. NO_3^- and NO_2^- were analyzed by ion chromatography method.

Fuzzy Comprehensive Assessment Method

In this study, fuzzy comprehensive assessment method was applied for overall water quality assessment. The delineation of influences from multifarious factors is one of the problems in the conventional methods for assessing the water quality. Fuzzy comprehensive method can solve this problem properly

and has been successfully used by Wang et al. (2017), Dahiya et al. (2007), and Kiurski-Milošević et al. (2015). The method is as follows:

The water quality grade (G_k) of each sample is determined by the appraising matrix ($B_{k \times m}$) illustrated as

$$B_{k \times m} = \begin{bmatrix} A^{(1)} \times R_{n \times m}^{(1)} \\ A^{(2)} \times R_{n \times m}^{(2)} \\ \vdots \\ A^{(k)} \times R_{n \times m}^{(k)} \end{bmatrix} = \begin{bmatrix} x_{11} & x_{12} & \dots & x_{1m} \\ x_{21} & x_{22} & \dots & x_{2m} \\ \vdots & \vdots & \dots & \vdots \\ x_{k1} & x_{k2} & \dots & x_{km} \end{bmatrix}, \quad (1)$$

$$G_k = g(x_{kg} = \max[x_{k1}, x_{k2}, \dots, x_{km}], 1 \leq g \leq m), \quad (2)$$

where k represents the number of samples; n represents the number of parameters; m represents the number of water quality grades; x_{kj} represents the weighted subordinate degree of sample k to grade m ; G_k represents the water quality grade of sample k ; $A^{(k)}$ is the weight vector, and it can be calculated by the following approach:

$$A^{(k)} = \begin{bmatrix} a_1^k \\ a_2^k \\ \vdots \\ a_n^k \end{bmatrix}, \quad (3)$$

$$a_i^k = \frac{\frac{c}{\sum_{j=1}^m s_{ij}}}{\sum_{i=1}^n \frac{c}{\sum_{j=1}^m s_{ij}}}, \quad (4)$$

where a_i^k represents the weight of the parameter i of the k th sample ($\sum_{i=1}^n a_i^k = 1$); c represents the concentration of a parameter of a given sample; s_{ij} represents the standardized concentration of parameter i of grade j ; and $R_{n \times m}^{(k)}$ is the subordinate degree matrix which can be determined by subordinate function (SF) (Wang et al. 2017). In water quality assessment, trapezoidal SF (Kiurski-Milošević et al. 2015) is commonly used to determinate the parameter subordinate degree to each water quality grade. The subordinate degree matrix is established as

$$R_{n \times m}^{(k)} = \begin{bmatrix} r_{11} & r_{12} & \dots & r_{1m} \\ r_{21} & r_{22} & \dots & r_{2m} \\ \vdots & \vdots & \dots & \vdots \\ r_{n1} & r_{n2} & \dots & r_{nm} \end{bmatrix}, \quad (5)$$

where r_{ij} represents the subordinate degree of parameter i to grade j , and is calculated using the following SF equations: When $i = 1$,

$$r_{ij} = \begin{cases} 1, & c \leq s_{ij} \\ \frac{s_{i(j+1)} - c}{s_{ij} - s_{i(j+1)}}, & s_{ij} < c \leq s_{i(j+1)} \\ 0, & c > s_{i(j+1)} \end{cases} \quad (6)$$

When $i = 2, 3, \dots, m - 1$,

$$r_{ij} = \begin{cases} 0, & c \leq s_{i(j-1)} \\ \frac{c - s_{i(j-1)}}{s_{ij} - s_{i(j-1)}}, & s_{i(j-1)} < c < s_{ij} \\ 1, & c = s_{ij} \\ \frac{s_{i(j+1)} - c}{s_{i(j+1)} - s_{ij}}, & s_{ij} < c \leq s_{i(j+1)} \\ 0, & c > s_{i(j+1)} \end{cases} \quad (7)$$

And when $i = m$,

$$r_{ij} = \begin{cases} 0, & c \leq s_{i(j-1)} \\ \frac{c - s_{i(j-1)}}{s_{ij} - s_{i(j-1)}}, & s_{i(j-1)} < c \leq s_{ij} \\ 1, & c > s_{ij} \end{cases} \quad (8)$$

($i = 1, 2, \dots, n; j = 1, 2, \dots, m$)

Health Risk Assessment

Health risk assessment is of great importance to support water quality assessment and management. Contaminants in water may pose health risks to human bodies through diverse pathways, the most common of which is drinking water intake. The assessment models recommended by the Ministry of Environmental Protection of the People’s Republic of China (2014) were selected to quantify the health risks from drinking water intake in this study. Cr^{6+} and NO_3^- are the major contaminants considered. The model for non-carcinogenic risk from drinking water intake is calculated as follows:

$$I_{oral} = \frac{C \times IR \times EF \times ED}{MT \times MW}, \quad (9)$$

$$HQ_{oral} = \frac{I_{oral}}{RfD_{oral}}, \quad (10)$$

where I_{oral} represents the daily average exposure dosage through oral exposure pathway per unit weight, (mg/(kg day)). C represents the concentration of the contaminant in groundwater determined by lab analysis, (mg/L). IR represents the drinking water intake rate, (L/day). EF and ED represent, respectively, the exposure frequency (d/a) and the exposure duration, (a). MT represents mean time of the non-carcinogenic effects, (day). MW represents the mean weight of the residents, (kg). HQ_{oral} and RfD_{oral} represents, respectively, the hazard quotient and the reference dosage,

[mg/(kg day)], for non-carcinogenic contaminants through oral exposure pathway.

In this study, 1.5 and 0.7 L/day were selected as the values of IR for adults and children, respectively; EF is 365 days per year and ED is 30 years for adults and 6 years for children; MW is 15 kg for children, 55 kg for female, and 75 kg for male; MT of non-carcinogenic effects on adults and children are 10,950 and 2190 days, respectively (Li et al. 2016a). The RfD_{oral} values for Cr^{6+} and NO_3^- are 0.003 mg/(kg day) and 1.6 mg/(kg day), respectively (Li et al. 2016a; Wu and Sun 2016; Ministry of Environmental Protection of People's Republic of China 2014).

After calculating the hazard quotients of Cr^{6+} and NO_3^- for the oral exposure pathway, the total non-carcinogenic risks can be calculated as

$$HI_{oral} = HQ_{oral,Cr^{6+}} + HQ_{oral,NO_3^-}, \quad (11)$$

where HI_{oral} represents the hazard index; $HQ_{oral,Cr^{6+}}$ and HQ_{oral,NO_3^-} represents the hazard quotient of Cr^{6+} and NO_3^- through oral exposure pathway, respectively. Non-carcinogenic risk denotes potential toxicity of non-carcinogenic contaminants such as nitrate and fluoride on human health through various exposure pathways. And one of the most common indices to assess the non-carcinogenic effects of non-carcinogenic contaminants is HQ. Additionally, the HQ and HI values exceeding 1 are considered unsafe for human health. (Ministry of Environmental Protection of People's Republic of China 2014; Li et al. 2016a).

Additionally, Cr^{6+} contamination can also result in carcinogenic risk through drinking water intake, which can be assessed by

$$CR_{oral} = I_{oral} * S, \quad (12)$$

where CR_{oral} denotes the carcinogenic risks via oral exposure pathway. S is the slope factor of the carcinogenic contaminants, [(mg/(kg day))⁻¹]. The value of S is set at 0.5 (mg/(kg day))⁻¹ for Cr^{6+} (Ministry of Environmental Protection of the People's Republic of China). The exposure duration (ED) is set at 25,550 days (70 years), implying the carcinogenic effects from Cr^{6+} on human body will last life-long (Li et al. 2016a).

Results and Discussion

Groundwater Chemistry

Physicochemical Parameter

The physicochemical parameters of the groundwater samples, including pH, $Na^+ + K^+$, Ca^{2+} , Mg^{2+} , Cl^- , HCO_3^- , SO_4^{2-} , NO_3^- , NO_2^- , TDS, TH, and Cr^{6+} , are listed in

Table 2. As shown in Table 2, pH values of groundwater from the Huanhe Formation range from 7.7 to 8.3, indicating alkaline water in nature. The pH values of all water samples fall within the limit prescribed by the *Standard for groundwater quality* (General Administration of Quality Supervision, Inspection & Quarantine of China and Standardization Administration of China 2017).

TDS and TH values of groundwater range from 504 to 2266 and 123 to 896 mg/L, respectively, with 9 and 12 samples exceeding the limits recommended by the *Standard for groundwater quality* for drinking purpose. For TDS, the over-limit samples are mainly distributed in the northeast of Changguanmiao Village, the east of Miaogou Village, and the west of Wuqi Town. The high TH samples are generally located in the Miaogou Village, Wangwazi Village, Tiebiancheng Town, and northeast of Changguanmiao Village. The mean value of TDS is 1253 mg/L, indicating that the groundwater in this area is generally saline water. The mean value of TH is 437 mg/L, which falls within the limit for drinking purpose (450 mg/L), indicating that the mixing can effectively reduce the level of TH.

In terms of cations, the $Na^+ + K^+$ concentration of the samples ranges from 77.1 to 640.2 mg/L, with a mean value of 330.4 mg/L. The high concentration of $Na^+ + K^+$ in the study area may be ascribed to cation exchange and the dissolution of silicates such as albite. Ca^{2+} and Mg^{2+} are the two common cations in groundwater. The concentrations of Ca^{2+} and Mg^{2+} range from 36.1 to 170.3 and 13.4 to 109.4 mg/L, with the mean values of 71.1 and 44.7 mg/L, respectively. The concentrations are acceptable for drinking purpose according to the Chinese standard for drinking water quality. Overall, compared to Ca^{2+} and Mg^{2+} , higher $Na^+ + K^+$ concentration has been observed in groundwater of Huanhe formation in the study area, and based on the mean concentrations, the order of cations is $Na^+ + K^+ > Ca^{2+} > Mg^{2+}$.

For anions, the concentrations range from 24.8 to 744.5 mg/L for Cl^- , 67.1 to 402.7 mg/L for HCO_3^- , and 110.5 to 888.6 mg/L for SO_4^{2-} , with mean values of 320.5, 227.4, and 417.0 mg/L, respectively. The Chinese standard for drinking water quality sets the acceptable limit of Cl^- and SO_4^{2-} for drinking water as 250 mg/L. Among the thirty samples, 18 samples exceed the acceptable limit for Cl^- and 20 samples exceed the limit for SO_4^{2-} . Based on the mean concentrations, the order of anions for all samples is $SO_4^{2-} > Cl^- > HCO_3^-$.

The main non-carcinogenic and carcinogenic contaminants in the study area are NO_3^- , NO_2^- , and Cr^{6+} . The NO_3^- concentration ranges from ND (not detectable) to 166.6 mg/L, with an average of 26.8 mg/L. The mean concentration of NO_2^- is 0.099 mg/L, with the maximum being 0.64 mg/L. For Cr^{6+} , the maximal concentration is 0.097 mg/L, and the mean is 0.020 mg/L. The national

Table 1 Groundwater physiochemical parameters

Index	Number	Unit	Maximum	Minimum	Mean	National standard (Grade III)	Total number exceeding standards
pH	30	–	8.3	7.7	8.0	6.5–8.5	0
Na ⁺ +K ⁺	16	mg/L	640.2	77.1	303.4	–	–
Ca ²⁺	16	mg/L	170.3	36.1	71.1	–	–
Mg ²⁺	16	mg/L	109.4	13.4	44.7	–	–
Cl ⁻	30	mg/L	744.5	24.8	320.5	250	18
HCO ₃ ⁻	16	mg/L	402.7	67.1	227.4	–	–
SO ₄ ²⁻	30	mg/L	888.6	110.5	417.0	250	20
NO ₃ ⁻	30	mg/L	166.6	ND	26.8	20	9
NO ₂ ⁻	16	mg/L	0.640	0.001	0.099	1.00	0
TDS	16	mg/L	2266	504	1253	1000	9
TH	30	mg/L	896	123	432	450	12
Cr ⁶⁺	30	mg/L	0.097	ND	0.020	0.05	3

ND not detectable

drinking water quality standards set the acceptable limit of NO₃⁻, NO₂⁻, and Cr⁶⁺ for drinking purposes as 20, 1.00, and 0.05 mg/L, respectively. As shown in Table 1, over one-third of the water samples are unsuitable for drinking due to contamination of NO₃⁻, and about 10% of the samples are contaminated by Cr⁶⁺.

Hydrogeochemical Type of Groundwater

Piper diagram (Piper 1944) is generally used to study the hydrogeochemical types of groundwater that are governed by major cations and anions in groundwater. As shown in Fig. 3, the samples are mostly plotted in zone B and D in the lower left triangle, indicating that the groundwater in the study area is mainly of “non-dominant” and “sodium” types. The samples are plotted in zone B, E, and G in the lower right triangle, suggesting non-dominant type, bicarbonate type, or chloride type. However, almost all samples are plotted in zone 1, 2, and 3, demonstrating that groundwater in the study area is mainly of SO₄·Cl–Na type, SO₄·Cl–Ca·Mg type, and/or HCO₃–Na type.

Natural Groundwater Volution Mechanisms

The Gibbs diagrams were developed by Gibbs in 1970 to quantitatively analyze the evolution of surface water, but now it is also widely applied in the studies of groundwater. Each of the Gibbs diagrams is divided into three parts, revealing three main evolution mechanisms: evaporation dominance, rock dominance, and precipitation dominance (Gibbs 1970). As shown in Fig. 4, most of the samples are plotted in the middle part of the diagrams, indicating that the leading factor influencing the groundwater chemistry is water–rock interactions and rock weathering. However,

there are also several samples plotted in the zone of evaporation dominance, suggesting that groundwater evaporation is also a noticeable factor affecting the groundwater chemistry. These samples are mainly located in the northeast of Changguanmiao Village and Xinzhai Village, where the main groundwater discharge zone is located. The shallow water level depth in the discharge zone makes groundwater evaporation important in influencing groundwater chemistry. Additionally, most samples show a slight increasing trend in the diagram, indicating again the impacts of evaporation.

Groundwater Quality Assessment

In this study, pH, TH, Cl⁻, SO₄²⁻, Cr⁶⁺, and NO₃⁻ were selected to appraise overall water quality using the fuzzy comprehensive method introduced above. According to the national groundwater quality standard (General Administration of Quality Supervision, Inspection and Quarantine of China and Standardization Administration of China 2017), groundwater quality is classified into five grades, grade I (excellent), grade II (good), grade III (fair), grade IV (poor), and grade V (very poor). The assessment results are listed in Table 2.

Table 2 shows that only one sample is classified as excellent quality water and nine samples are classified as good quality water, and these samples are suitable for multiple purposes. Nine samples are classified as fair quality, which are considered marginally acceptable for drinking and need certain pretreatment for domestic uses. Eight samples are classified as poor quality water and three samples are classified as very poor quality water. The poor quality water is unsuitable for drinking purpose, but can be used for irrigation if the irrigation pattern and vegetation types fit. The very poor quality water is generally

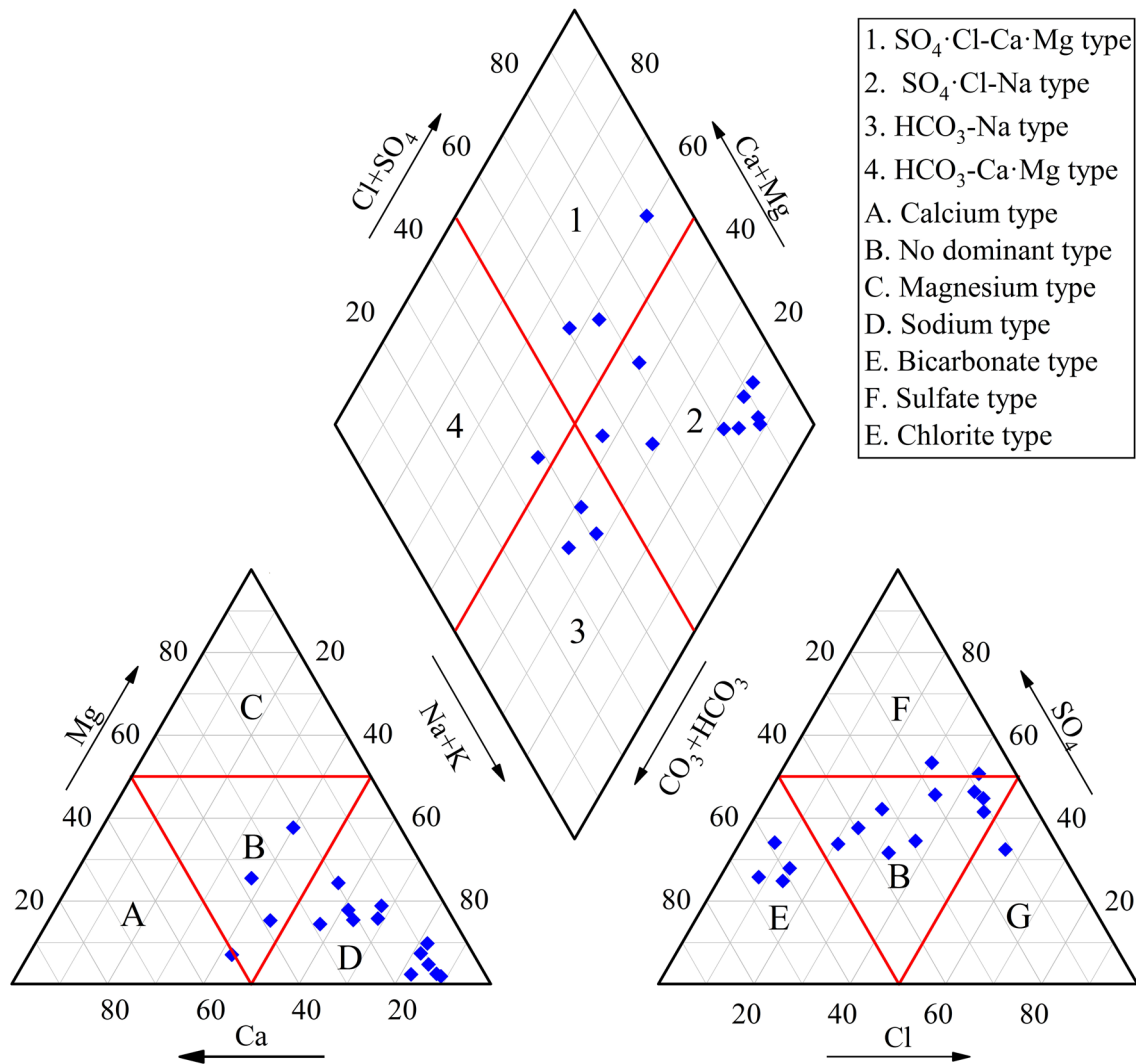


Fig. 3 Piper diagram showing the hydrochemical types of groundwater

unsuitable for all purpose, but after deep treatment it may be used for recreation and irrigation. The poor or very poor quality water samples were mainly collected in the middle, west, and south parts of the study area where it is associated with main contaminants such as SO_4^{2-} , Cr^{6+} , and NO_3^- . As shown in Fig. 5, the whole study area is covered by poor and very poor quality water (grades IV and V) in terms of SO_4^{2-} , except in Xuecha Village and in the northwest of Wugucheng Village where fair quality (classified as grade III) can be locally seen. According to the borehole data, there is a gypsum horizon at the depth around 100 m in the study area, which may be responsible for high concentration of SO_4^{2-} in study area (Gu et al. 2015). In terms of Cr^{6+} , the study area generally belongs to the fair water quality (grade III) zone except in Changguanmiao Village and Miaogou Village where groundwater is poor due to contamination of Cr^{6+} . As agriculture is

common and around 1120 tons of nitrogenous fertilizer is used per annum over the entire county (Shaanxi Provincial Bureau of Statistics & NBS Survey Office in Shaanxi 2017), NO_3^- contamination is prevalent. The entire study area is covered by poor and very poor quality water in terms of NO_3^- except some local fair water quality zones.

Health Risks Assessment

The results of Health risk assessment are shown in Fig. 6. For children, the hazard index (HI_{oral}) ranges from 0.061 to 5.637 with a mean value of 1.023. Ten samples have HI_{oral} exceeding 1, indicating that the Cr^{6+} and NO_3^- of most water samples cause little non-carcinogenic health risks to children through oral pathway. For female adults, the HI_{oral} ranges from 0.036 to 3.294 with the mean of 0.598. Only six samples (20% of the samples) have HQ_{oral} exceeding 1, which

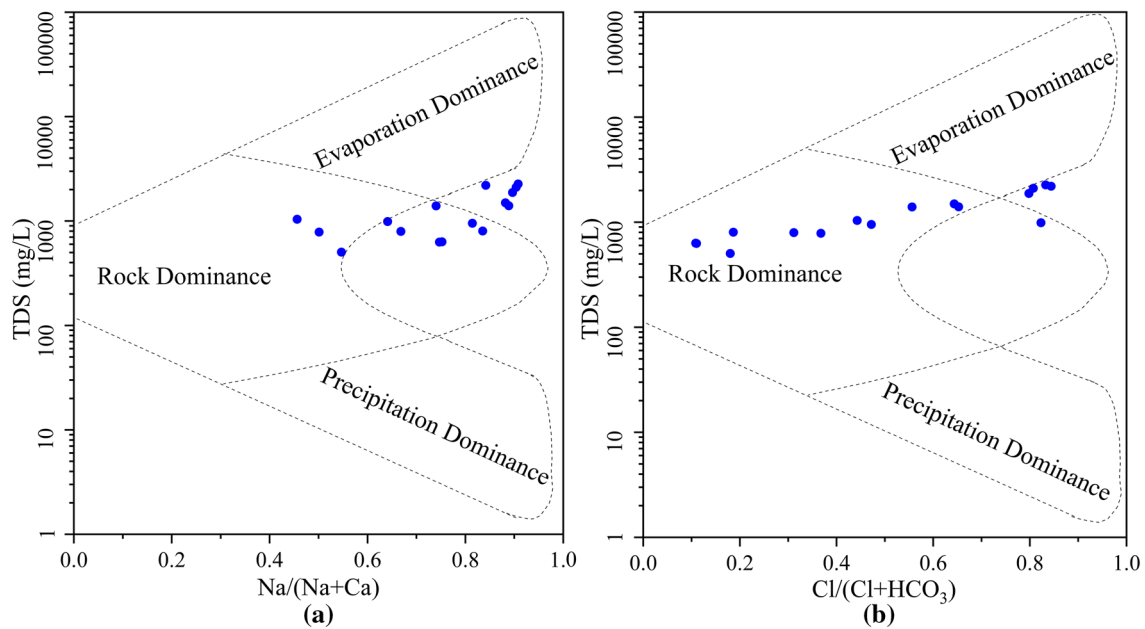


Fig. 4 Gibbs diagram indicating the mechanisms of groundwater chemistry evolution

means that most samples cause little non-carcinogenic health risks through oral pathway. For male adults, the HI_{oral} ranges from 0.026 to 2.416 with the mean of 0.438. Only two samples have HI_{oral} exceeding 1, which means that most samples can cause little non-carcinogenic health risks to male through oral exposure pathway. The mean value of HI_{oral} for children is higher than 1, while that for female and male adults are both lower than 1, indicating that the mixing of groundwater can significantly reduce the non-carcinogenic risks to local adults but contributes less to reduce the non-carcinogenic risks of children.

The carcinogenic risks from Cr^{6+} for local residents are significantly lower than non-carcinogenic risks (Fig. 6). The carcinogenic risks from Cr^{6+} through oral exposure pathway (CR_{oral}) for children range from 1.17×10^{-4} to 2.26×10^{-3} with a mean of 6.94×10^{-4} . It is much higher than the acceptable limit of 1×10^{-6} (Ministry of Environmental protection of the People's Republic of China 2014). The CR_{oral} values for female and male adults range from 6.82×10^{-5} to 1.32×10^{-3} and 5.00×10^{-5} to 9.70×10^{-4} , with means of 4.05×10^{-4} and 2.97×10^{-4} , respectively. The risks also exceed the limit, revealing that the residents in the study area suffer from high carcinogenic risks caused by Cr^{6+} in groundwater through drinking water intake. Particularly, suggested by the mean values of CR_{oral} , the carcinogenic risk of children is higher than that of female adults and male adults. This is also supported by the results of Wu and Sun (2016) and Li et al. (2016a).

Overall, adults in the study area face acceptable non-carcinogenic risks, while children face unacceptable

non-carcinogenic risks from Cr^{6+} and NO_3^- in groundwater through drinking water intake. Both children and adults face unacceptable carcinogenic risks caused by Cr^{6+} . The reason why children face higher carcinogenic risks through oral exposure pathway than females and males may be attributed to the lower body weight of children than adults. The results are consistent with other studies (Li et al. 2016a, 2018d; Su et al. 2013; He et al. 2011).

The study results are valid and meaningful for groundwater exploitation and management, despite some uncertainties, which mainly include model uncertainty, parameter uncertainty, and input data uncertainty (Li et al. 2016a). The health risk assessment results represent mean risks of the groundwater in study area, and the specific risk for each individual varies around the mean values.

Conclusions

In this study, thirty groundwater samples were collected and analyzed for physicochemical parameters. Groundwater chemistry was delineated by Piper diagram and Gibbs diagrams, and fuzzy comprehensive method was used to assess the groundwater quality. Health risks from Cr^{6+} and NO_3^- through drinking water intake were assessed. The main conclusions are summarized as follows:

Groundwater in the study area is slightly alkaline, with TDS and TH ranging from 504 to 2266 and 123 to 896 mg/L, respectively. Groundwater in the study area is mainly of

Table 2 Results of water quality assessment using fuzzy comprehensive method

Sample	Subordinate degree					Grade	Water quality
	$m=I$	$m=II$	$m=III$	$m=IV$	$m=V$		
wk8	0.000	0.119	0.074	0.309	0.498	V	Very poor
w48	0.000	0.084	0.321	0.570	0.025	IV	Poor
wk7	0.044	0.174	0.125	0.479	0.164	IV	Poor
wk10	0.019	0.241	0.134	0.537	0.069	IV	Poor
w74	0.009	0.287	0.066	0.592	0.045	IV	Poor
wk6	0.190	0.299	0.118	0.189	0.205	II	Good
wk5	0.159	0.312	0.136	0.204	0.190	II	Good
w73	0.120	0.608	0.114	0.138	0.020	II	Good
wm2	0.017	0.300	0.648	0.035	0.000	III	Fair
wm1	0.387	0.532	0.081	0.000	0.000	II	Good
wk4	0.039	0.599	0.362	0.000	0.000	II	Good
wk1	0.270	0.475	0.255	0.000	0.000	II	Good
wk3	0.000	0.219	0.416	0.348	0.018	III	Fair
wk2	0.073	0.296	0.473	0.134	0.024	III	Fair
xk3	0.000	0.060	0.389	0.188	0.363	III	Fair
xk9	0.360	0.558	0.082	0.000	0.000	II	Good
w110	0.226	0.138	0.009	0.487	0.140	IV	Poor
tw11	0.044	0.094	0.336	0.291	0.234	III	Fair
w119	0.000	0.170	0.371	0.262	0.197	III	Fair
1	0.000	0.199	0.391	0.351	0.059	III	Fair
w106	0.000	0.241	0.264	0.478	0.016	IV	Poor
wk9	0.231	0.057	0.329	0.383	0.000	IV	Poor
w122	0.159	0.205	0.009	0.171	0.456	V	Very poor
w29	0.231	0.238	0.137	0.298	0.095	IV	Poor
tw104	0.534	0.325	0.141	0.000	0.000	I	Excellent
y11	0.000	0.289	0.084	0.252	0.375	V	Very poor
6	0.029	0.169	0.402	0.240	0.160	III	Fair
w45	0.381	0.515	0.104	0.000	0.000	II	Good
7	0.065	0.465	0.470	0.000	0.000	III	Fair
w14	0.239	0.358	0.009	0.257	0.136	II	Good

SO₄·Cl–Na, SO₄·Cl–Ca·Mg, and HCO₃–Na types, which are mainly governed by rock weathering and rock–water interactions. However, evaporation also plays a minor role in influencing the groundwater chemistry.

According to the water quality assessment results, 63.33% of the groundwater samples are of excellent or good or fair quality and are acceptable for drinking and irrigation purposes. The remaining 36.67% of the groundwater samples are in poor or very poor quality, and are not acceptable for drinking purpose. The excellent, good and fair quality samples were mainly collected from Xuecha Village, Loufangping Village, and Tiebiancheng Town, which are recommended to be the water-source region for the study area. The poor and very poor quality samples were mainly collected

from densely populated regions and groundwater may be polluted by the urbanization and human activities.

The non-carcinogenic risks of female and male adults in the study area caused by Cr⁶⁺ and NO₃[−] through oral exposure pathway are generally acceptable, but that of children is unacceptable. The carcinogenic risks caused by Cr⁶⁺ are high and unacceptable for both children and adults. The mean values of carcinogenic risks from Cr⁶⁺ in groundwater are 6.94×10^{-4} for children, 4.05×10^{-4} for female adults, and 2.97×10^{-4} for male adults, respectively. Additionally, children face higher carcinogenic risks compared with adults because of lower body weight than adults.

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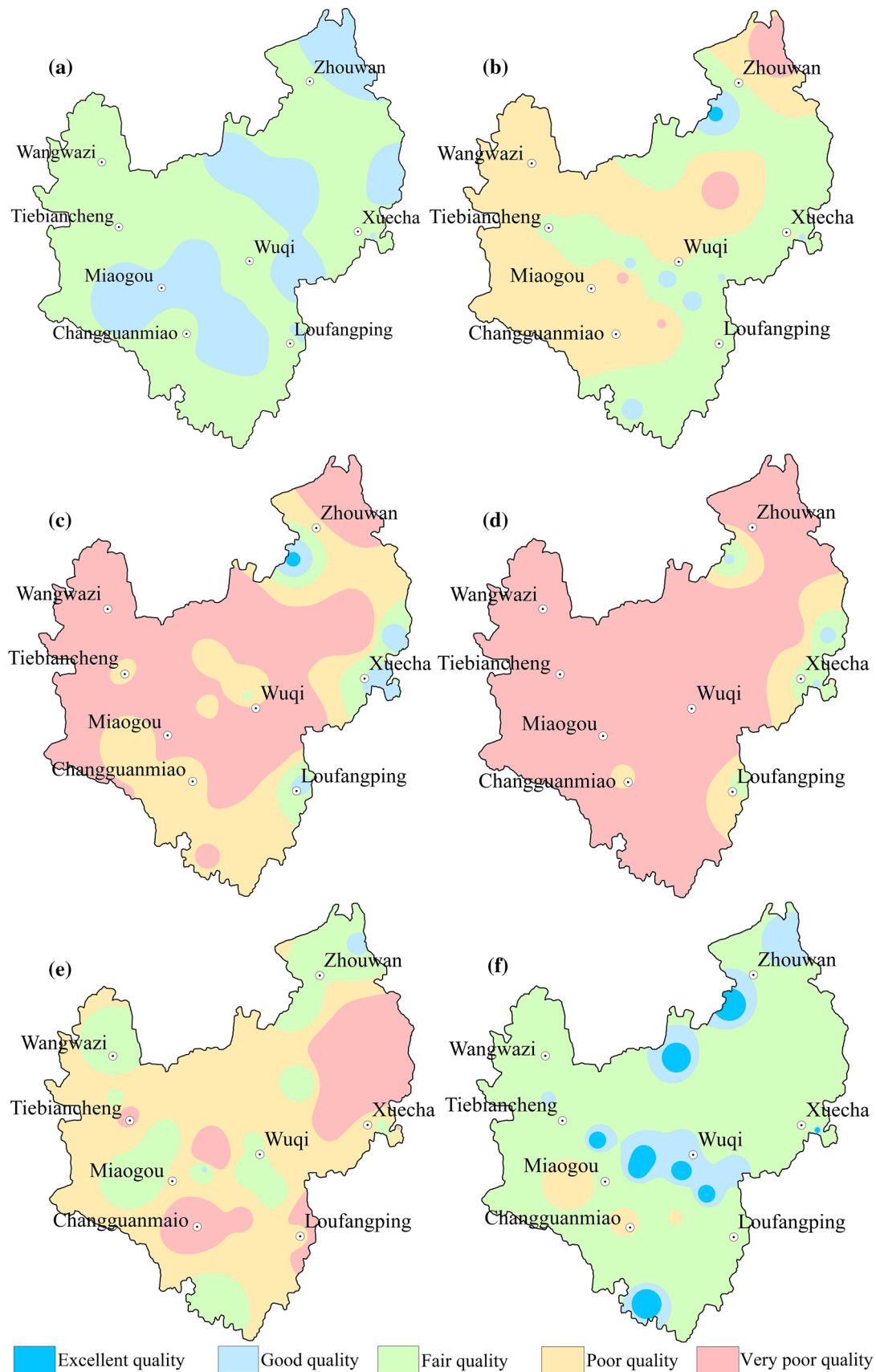
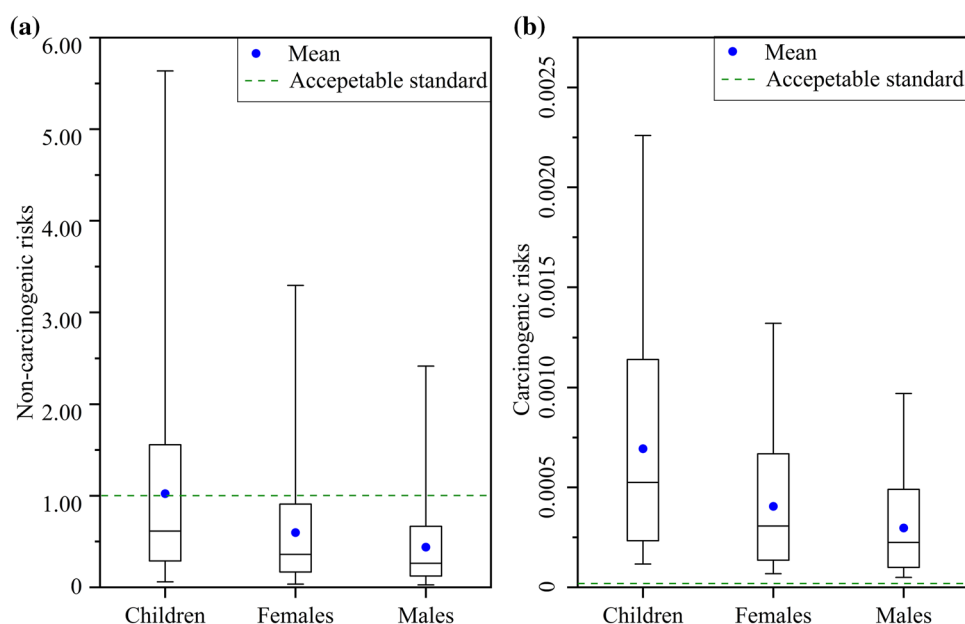


Fig. 5 Spatial distribution of contaminants: **a** pH, **b** TH, **c** Cl⁻, **d** SO₄²⁻, **e** NO₃⁻, and **f** Cr⁶⁺

Fig. 6 Boxplots showing the results of health risks assessment: **a** non-carcinogenic risks and **b** carcinogenic risks



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