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ORIGINAL PAPER

Occurrence, Species, and Health Effects of Groundwater Arsenic in Typical Rural Areas Along the Northern Foot of the Qinling Mountains, China

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Abstract

This research focused on the major water quality parameters and trace elements in 73 groundwater samples collected from some rural areas at the northern foot of Qinling Mountains, and the hydrochemical characteristics of groundwater in this area were investigated. The distribution and enrichment of arsenic (As) in groundwater were specifically explored, the different chemical species of arsenic were calculated using PHREEQC, and the carcinogenic and non-carcinogenic health risks caused by total arsenic were assessed using probabilistic models. The results showed that the concentration of arsenic in groundwater ranged within 1.46–8.69 μg/L, which is close to the World Health Organization's guideline value recommended for drinking water (10 μg/L). The chemical species of arsenic simulated using the PHREEQC model showed that the main species of arsenic in most groundwater samples in the study area were $HAsO_4^{2-}$ and $H_2AsO_4^{-}$, while the main species of arsenic in a few samples were H_3AsO_3, followed by H_3AsO_4, AsO_4^{3-}, AsO_3^{3-}, $HAsO_3^{2-}$, and $H_4AsO_3^{+}$, which were present in a relatively small proportion. Changes in environmental acidity and redox conditions had significant effects on the species of arsenic present in groundwater. The results of the health risk assessment showed that the non-carcinogenic risk of human health due to exposure to arsenic is 3.19×10^{-5} and 1.11×10^{-4} for adults and children, respectively. Children are at greater health risk than adults.

Keywords Arsenic in groundwater · Chemical species · Probabilistic health risk · Groundwater quality · Rural areas

Introduction

Arsenic (As) is a common contaminant in groundwater. It is the 20th most abundant element in the crust of the Earth (Villalba et al. 2020). Arsenic contamination in groundwater is a global threat, with more than 20 countries including China (Guo et al. 2008; Zhang et al. 2017), Thailand (Tiankao and Chotpantarat 2018), India (Khan et al. 2022; Sridharan and Nathan 2018), Bangladesh (Huq et al. 2020; Islam et al. 2022), the United States (Gong et al. 2014), Mexico (Rodriguez-Cantu et al. 2022), Argentina (Alcaine et al. 2020), and Pakistan (Shahid et al. 2018a, b) reporting arsenic poisoning in drinking water (He and Charlet 2013). Particularly, the situation of arsenic poisoning in drinking water in China is serious. As early as in the 1980s, Xinjiang, the biggest provincial administrative government in China, reported its first case of arsenic poisoning from drinking water (Wang et al. 1983). Later, large-scale arsenic poisoning in drinking water were reported in Shanxi and Inner Mongolia (Guo et al. 2014; Sun 2004). At present, these provinces are still among the most serious arsenicosis-stricken provinces in China (He et al. 2020). Long-term intake of arsenic-contaminated groundwater can cause skin pigmentation, hyperkeratosis, ulcers, and can threaten the health of internal organs such as the liver, kidneys, and lungs (Shaji et al. 2021), and severe arsenic poisoning can even lead to skin and lung cancers (Rasheed

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et al. 2017). It is reported that in the West Bengal, India, endemic arsenic poisoning has not only endangered the lives and health of millions of people, but also adversely affected their offspring through genetic means (Bhowmick et al. 2018). The International Agency for Research on Cancer (IARC) classified arsenic as a Class 1 human carcinogen (IARC 2011). Earlier, the permissible value of arsenic in drinking water was set as 50 μg/L, but due to the serious health threat of arsenic the World Health Organization (WHO) changed the maximum permissible value of arsenic in drinking water to 10 μg/L (WHO 1993).

The main sources of arsenic in groundwater are geological formations (e.g., sediments/rocks, soil, and volcanic rocks) (Kim et al. 2012; Kumar et al. 2016; Santha et al. 2022), geothermal activities (Bundschuh and Maity 2015), coal mining (Cao et al. 2021), and anthropogenic factors (Li et al. 2020; Nottebaum et al. 2020). The presence of arsenic in groundwater is associated with host minerals, as well as the redox state and pH in the aquatic environments (Chakraborty et al. 2015), making arsenic a redox sensitive element (Carraro et al. 2015; Chakraborty et al. 2022; Meng et al. 2003). Arsenic in natural water exists as inorganic form, while organic form of arsenic tends to be low in natural groundwater (Park et al. 2023; Schreiber 2021). The most common chemical species of arsenic in natural water are As(III) and As(V), and As(III) is often considered more toxic than As(V) due to its ability to bind to sulfhydryl groups, thereby affecting the function of proteins (NRC 1999). Therefore, gaining specific knowledge of the chemical species and distribution of arsenic in groundwater can be helpful for the reduction in the human health risk. In this regard, many scientific papers have been published to reveal the occurrence, migration, and affecting factors of different species of arsenic in groundwater. Among the existing research, Cao et al. (2022) revealed the spatiotemporal variability of groundwater arsenic under the long-term groundwater abstraction conditions, and this research demonstrated that groundwater abstraction could severely alter the biogeochemical environments in which the enrichment of groundwater arsenic might be significantly different. Ke et al. (2022) focused on the arsenotrophic microbiome in groundwater, and their research suggested that the diversities of bacteria are higher in high arsenic groundwater than in low arsenic groundwater, and the concentrations of SO_4^{2-} and arsenic and the levels of oxidation–reduction potential (ORP) and pH are important factors affecting the groundwater microbial populations. In addition, Li et al. (2022) showed that the intensive irrigation in agricultural areas would benefit the release of arsenic into groundwater. These recent studies have tremendously help researchers to better understand the mechanisms of groundwater arsenic enrichment and migration.

The rural areas at the northern foot of the Qinling Mountains are critical for maintaining the sustainability of society development in and around the Xi'an City, the capital city of Shaanxi Province in China, because the Golden Basin Reservoir in these areas provides fresh water supply for the southern part of the Xi'an City. Groundwater, however, is of particular importance to the people living in rural areas (Xu et al. 2023). Numerous scholars have conducted many studies on nitrogen, fluoride, and arsenic contamination of groundwater in different parts of the Guanzhong Plain (Li et al. 2014a; Li et al. 2023; Luo et al. 2014; Nsabimana et al. 2023; Wu and Sun 2016; Ren et al. 2021; Zhang et al. 2018, 2022a, 2022b; Wang and Li 2022). Wang et al. (2023) have recently investigated the impacts of climate change on groundwater level in this area, benefiting the understanding into the mechanisms of groundwater system responses to external forces. However, this research did not consider the response of arsenic concentration to external forces. An early investigation in rural drinking water quality in the Huyi District, Xi'an, showed that arsenic exceeded the WHO and national standards of arsenic, indicating serious health risk to local residents (Chang et al. 2019). In addition, Qiao et al. (2020) quantified the health risk of groundwater in the Guanzhong Plain, and found that arsenic posed carcinogenic health risk and non-carcinogenic risk to humans. However, as the fourth biggest plain in northwest China, groundwater in the Guanzhong Plain is still not well studied for arsenic contamination, and the distribution and different chemical species of arsenic in groundwater as well as their effects on human health are not clear. Therefore, this study was conducted to (1) characterize the groundwater hydrochemistry and spatial distribution of arsenic in the area, (2) analyze the controlling factors that may affect arsenic enrichment in groundwater, (3) calculate the different chemical species of arsenic and analyze the main factors controlling the variation of arsenic speciation, and (4) estimate the probabilistic health risks caused by arsenic. The outcomes of this research may benefit local and regional protection and management of groundwater for drinking purpose, and this research can also act as a reference for other areas facing similar arsenic poisoning problems in the world.

Materials and Methods

Study Area

The study area is located in central part of the Guanzhong Plain, Shaanxi Province, China bordered by the Qinling Mountains in the south, and Wei River in north. It covers four main county-level administration regions, i.e., Yangling District of Xianyang City, Mei County, Zhouzhi County, and Huyi District of Xi'an City (Fig. 1). With elevations

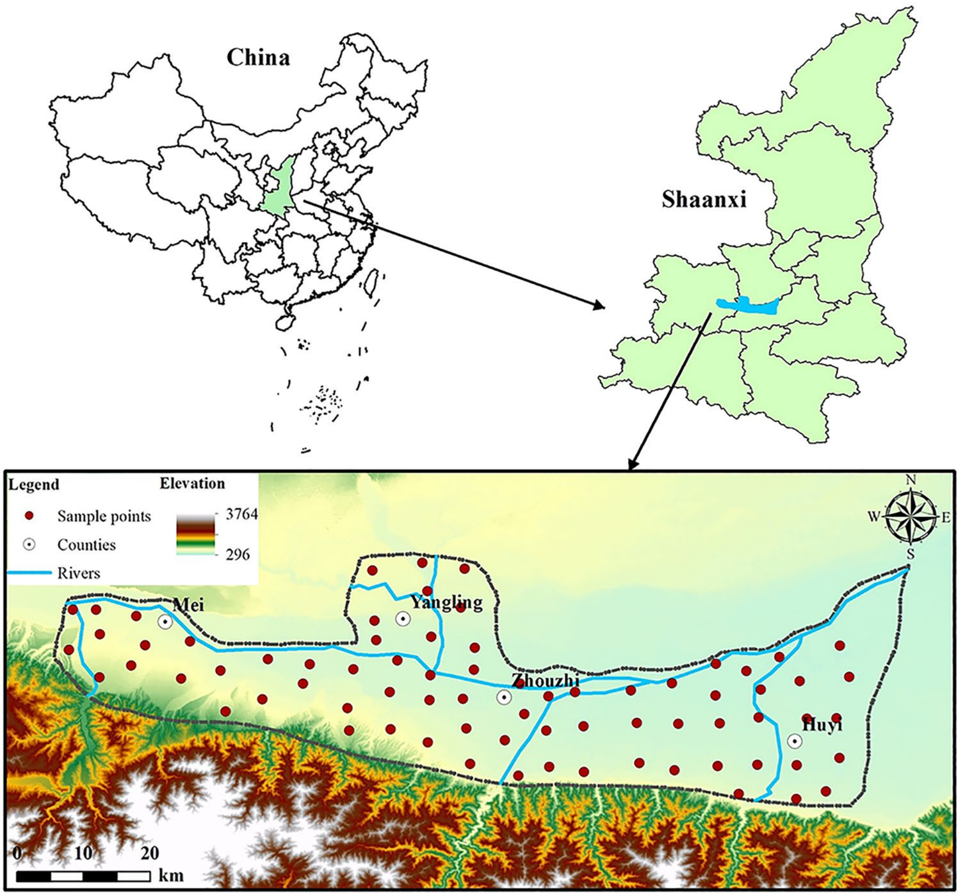


Fig. 1 Location of study area and sampling sites

ranging from 370 to 1200 m, the study area has a generally high elevation in the south and a low elevation in the north. The landform types include the Qinling Mountains, Loess Plateau, and Wei River Plain. This study area has a warm-temperate continental monsoon climate with a cold and dry winter, but a very hot and rainy summer (Yang et al. 2022). Due to the influence of landscape, the climate of the mountainous areas and plains varies significantly from north to south. The average annual temperature is 13.2 °C, with January being the coldest month and July the hottest (Wang and Li 2022; Zhou et al. 2022). Precipitation shows a decreasing trend from south to north, showing large regional differences, intra-annual variations and inter-annual variations. The average annual precipitation is 700–900 mm in the mountainous areas, but is 500–700 mm in the plains (Wang et al. 2023).

The study area is mostly a low-lying fault basin, and there is a wide distribution of Quaternary loose sediments with a thickness of several hundred meters in the area. The Quaternary loose sediments are permeable and can be easily recharged by precipitation and rivers, thus containing rich groundwater resources (Nsabimana et al. 2022). Influenced by surface topography, groundwater in the area is mainly discharged horizontally, from south to north towards the Wei River (Wang et al. 2023). The water-bearing formation is mainly the Quaternary loose sedimentary layers which are widely distributed and continuous throughout the region. The water-rich areas are mainly distributed along the Wei River and its tributaries as well as in the pluvial fans in front of the Qinling Mountains (Nsabimana and Li 2022). On the contrary, the Loess Plateau has weaker groundwater abundance due to its poor geological and hydrogeological conditions. Controlled by topography, groundwater flows generally from the Qinling Mountains to the Wei River in the south of the study area, and from the Loess Plateau to the Wei River in the north of the study area (Zhang et al. 2022a). Groundwater in this area is recharged widely by precipitation, but river percolation, irrigation infiltration, and lateral inflow are also important ways of groundwater getting recharged (Zhang et al. 2022b). On the contrary, groundwater in this area is primarily discharged by evaporation, artificial abstraction, and lateral outflow.

Sample Collection and Analyses

For this research, groundwater samples were collected in July 2021 from 73 shallow domestic water wells in the rural areas of the study area, and the sampling locations are shown in Fig. 1. The sampling sites were selected in major villages to reflect the rural groundwater quality, thus these sampling sites were distributed uniformly in the study area. The procedures of sampling, storage, and handling strictly followed the national standards (Ministry of Environmental Protection of the P.R. China 2020). Before the samples were collected, the wells were pumped for 5–10 min, after which the sampling containers were rinsed three times with the water to be taken. Parameters that can be easily changed such as pH, conductivity, and ORP were measured directly in the field using portable pH test device, portable conductivity test device, and portable ORP test device. All the portable devices were calibrated before sampling using calibration liquids. Other indicators were sent to the laboratory of the Mineral Resources Investigation Center of the China Geological Survey in Xi'an for further analysis. All tests followed the national technical regulations (Ministry of Land and Resources of the P. R. China 2006). Among the parameters analyzed, K^+, Na^+, Ca^{2+}, Mg^{2+}, F^-, NO_2^-, and NO_3^- were measured by ion chromatography. HCO_3^-, Cl^-, CO_3^{2-}, and SO_4^{2-} were measured by titration. TDS was measured by drying and weighing method. Fe and Mn were determined by plasma emission spectrometry. Arsenic was determined using atomic fluorescence spectrometry. Cr^{6+} was determined using UV–Vis spectrophotometry. All the instruments for the physicochemical analyses were pre-calibrated to ensure the reliability of the analyses. In addition, the analyses were carried out through blank samples and triplicates. To ensure the accuracy of the data, the percentage error of ion balance (%CBE) was also calculated for all water samples after the physicochemical analyses (Eq. 1), and the results indicated that over 95% of the samples had an analytical error less than ± 5%, and the highest analytical error is 6.2%, which proved the reliability of the analyzed data.

$$\%\,\mathrm{CBE} = \frac{\sum \mathrm{Cations} - \sum \mathrm{Anions}}{\sum \mathrm{Cations} + \sum \mathrm{Anions}} \times 100\% \tag{1}$$

Human Health Risk Quantification

The USEPA model (USEPA 1989) was used to calculate the carcinogenic and non-carcinogenic health risks of arsenic for adults and children. Considering that drinking water intake was the most important exposure pathway, oral ingestion was considered in this research. In addition, groundwater was also used for washing hands and faces and shower, dermal contact was considered as the secondary exposure pathway, while other exposure pathways such as intake via food consumption and inhalation were ignorable (Wu et al. 2020). The health risk was calculated by the following equations (Li et al. 2019a, b):

The equation for calculating the exposure dose for oral ingestion is as follows:

$$\mathrm{CDI} = \frac{\mathrm{CW} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \tag{2}$$

where CDI is the chronic daily intake dose (mg/kg d); CW is the concentration of the contaminant in groundwater (mg/L); IR is the daily drinking water rate (L/d); EF is exposure frequency (d/a); ED is the exposure duration and this variable indicates the number of years during which the objects are exposed to the contaminants (a); BW is the body weight (kg); and AT is the average time of exposure (d). For non-carcinogenic risk assessment, $\mathrm{AT} = \mathrm{EF} \times \mathrm{ED}$, while for carcinogenic risk quantification, $\mathrm{AT} = \mathrm{EF} \times T$ (T is the average life span in the study area).

The equation for calculating the exposure dose for skin contact is as follows:

$$\mathrm{DAD} = \frac{\mathrm{DA}_{\mathrm{event}} \times \mathrm{EV} \times \mathrm{ED} \times \mathrm{EF} \times \mathrm{SA}}{\mathrm{BW} \times \mathrm{AT}} \tag{3}$$

where DAD is the dose of contaminant exposure by dermal contact (mg/kg d); $\mathrm{DA}_{\mathrm{event}}$ is the absorbed dose by dermal contact ($\mathrm{mg/cm}^2$); EV is the frequency of daily dermal contact events such as swimming, bathing, and washing (times/d); SA is the surface area of exposed skin (cm^2); ED, EF, BW, AT, and other parameters have the same meaning as those in Eq. (1). $\mathrm{DA}_{\mathrm{event}}$ can be calculated using the following equation:

$$\mathrm{DA}_{\mathrm{event}} = K_p \times \mathrm{CW} \times t_{\mathrm{event}} \times 10^{-3} \tag{4}$$

where K_p is the skin permeability coefficient for harmful substances (cm/h); t_{event} is the length of a single skin contact (h). The values for all variables are shown in Table 1, and the values were adjusted to fit the actual situation in China (Zhang et al. 2019a, b).

To calculate the carcinogenic risk, the following equation is usually used:

$$R = E \times \mathrm{SF} \tag{5}$$

where R is the carcinogenic risk index (dimensionless); E is the exposure dose (mg/kg d) to groundwater by oral intake or dermal contact, i.e., CDI or DAD; SF is the slope factor of the contaminants ($(\mathrm{mg/kg\ d})^{-1}$).

The total carcinogenic risk index (CR_i) can be calculated by summing the carcinogenic risk index of oral intake (R_o) and the carcinogenic risk index of dermal exposure (R_d) as follows:

$$\mathrm{CR}_i = R_o + R_d \tag{6}$$

Table 1 Exposure parameters for adults and children

Exposure route	Parameter	Units	Adult	Children	Data source
Oral intake	IR (Intake rate)	L/d	1.50	0.85	Zuo (2011)
	BW (Body weight)	kg	61.75	15.00	Zhang et al. (2019a, b)
	EF (Exposure frequency)	d/a	365	365	USEPA (2004)
	ED (Exposure years)	a	30	6	Zhang et al. (2019a, b)
Dermal intake	BW (Body weight)	kg	61.75	15.00	Zhang et al. (2019a, b)
	EF (Exposure frequency)	d/a	200	200	USEPA (2004)
	ED (Exposure duration)	a	30	6	Zhang et al. (2019a, b)
	AT (Non-carcinogenic exposure time)	d	ED × 365	ED × 365	USEPA (2004)
	AT (Carcinogenic exposure time)	d	74.68 × 365	10 × 365	Zhou and Zhang (2010)
	SA (Skin surface area)	cm^2	16,110	8650	Wang et al. (2008)
	EV (Daily exposure frequency)	d^{-1}	1	1	USEPA (2004)
	K_p (Skin permeability coefficient)	cm/h	0.001	0.001	USEPA (2004)
	t_{event} (Skin contact duration)	h	0.25	0.33	USEPA (2004)

The non-carcinogenic risk index is usually calculated using the following assessment model:

$$\mathrm{NCHQ} = E/\mathrm{RfD} \tag{7}$$

where NCHQ is the non-carcinogenic risk index (dimensionless); E is the groundwater exposure dose (mg/kg d) by oral intake or dermal contact route, i.e., CDI or DAD; RfD is the reference dose (mg/kg d).

The total non-carcinogenic risk index (HQ_i) can be expressed by summing the carcinogenic risk index of oral intake (NCHQ_o) and the carcinogenic risk index of dermal exposure (NCHQ_d) is as follows:

$$\mathrm{HQ}_i = \mathrm{NCHQ}_o + \mathrm{NCHQ}_d \tag{8}$$

Monte Carlo Simulation

In the traditional health risk assessment process, a specific value is used for the exposure parameter, while in reality these parameter values have some uncertainty (Ganyaglo et al. 2019). Monte Carlo simulation method is widely used to quantify the uncertainty associated with health risk models (Liu et al. 2022). It uses random sampling and statistical tests to obtain approximate solutions to the problem. This is done by simulating the generated random numbers based on the probabilistic process of constructing events from the probability distributions of the measured data. In this research, the Crystal Ball software was used to calculate the risk level for adults and children by performing 10,000 stochastic iterations. The procedures of Monte Carlo simulation include Define Assumptions, Define Predictions, Determine Run Preferences, and Run Simulation.

The probability distributions of total arsenic were fitted using Crystal Ball risk simulation software embedded in Microsoft Excel. In this software, different probability distributions for total arsenic can be automatically calculated, and then ranked by Anderson–Darling test. The P–P and Q–Q plots were inspected to determine if there is any systematic variation in the magnitude of residuals (Mondal and Polya 2008). The uncertainties of the model parameters of intake rate (IR), body weight (BW), and exposure frequency (EF) were considered according to the recommended value of the Ministry of Environmental Protection of the People's Republic of China (2014) and relevant studies conducted in China (Zhang et al. 2019a, b; Liu et al. 2022), and it was determined that IR showed a normal distribution, BW showed a log-normal distribution, and EF showed a triangular distribution. The distribution types of the pollutant and exposure parameters are shown in Table 2.

Results and Discussion

Basic Hydrochemical Characteristics

The water quality parameters of groundwater in the study area were statistically analyzed, and the maximum and minimum values, mean, median, standard deviation of all parameters considered in this study are shown in Table 3. These parameters were also compared with the national groundwater quality standards (General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China 2017), and the proportions of groundwater samples falling within each groundwater quality classification are also listed in Table 3. Table 3 shows that the pH value in the study area varied from 6.83 to 7.94, with a mean value of 7.44, indicating that

Table 2 Range of exposure parameters and contaminants concentration distribution

Indicators		Distribution types	
		Adult	Children
Exposure parameters	IR	Normal (1.50,0.15)	Normal (0.85,0.09)
	BW	Lognormal (61.75,6.18)	Lognormal (15.00,1.50)
	EF (Oral intake)	Triangular (180,345,365)	Triangular (180,345,365)
	EF (Dermal contact)	Triangular (180,200,220)	Triangular (180,200,220)
Contaminants	Total arsenic	Lognormal (0.00265,0.00115)	

Table 3 Statistics of water quality parameters

Parameters	Units	Minimum	Maximum	Average	Median	Standard deviation	Proportion of groundwater quality classification %				
							Class I	Class II	Class III	Class IV	Class V
Temperature	℃	16.1	26.9	19.0	18.6	2.3	–	–	–	–	–
pH	–	6.83	7.94	7.44	7.41	0.22	100	0	0	0	0
ORP	mV	-107	533	171	183	79	–	–	–	–	–
TDS	mg/L	262	2566	657	617	357	5.5	35.6	46.6	10.9	1.4
HCO_3^-	mg/L	125	642	289	275	98	–	–	–	–	–
Cl^-	mg/L	2.6	210.0	32.1	20.6	33.9	82.2	15.1	2.7	0	0
NO_3^-	mg/L	4.5	397.0	97.6	68.5	89.2	11.0	11.0	45.2	9.6	23.2
NO_2^-	mg/L	2.06	3.48	2.80	2.85	0.33	0	0	94.5	5.5	0
F^-	mg/L	0.040	0.703	0.197	0.162	0.130	100	0	0	0	0
SO_4^{2-}	mg/L	5.59	997.00	92.89	62.40	122.70	41.1	41.1	16.4	0	1.4
Na^+	mg/L	4.83	308.00	36.88	20.10	42.24	97.2	1.4	0	1.4	0
K^+	mg/L	0.48	28.10	2.45	1.94	3.22	–	–	–	–	–
Ca^{2+}	mg/L	30.4	220.0	114.7	110.0	45.2	–	–	–	–	–
Mg^{2+}	mg/L	9.19	161.00	29.91	21.60	21.85	–	–	–	–	–
Arsenic	μg/L	1.46	8.69	2.66	2.29	1.24	0	0	100	0	0
Fe	mg/L	0.02	9.60	0.49	0.07	1.42	68.5	8.2	2.7	16.5	4.1
Mn	μg/L	0.52	1417.00	101.11	2.51	237.46	83.5	0	1.4	15.1	0
Cr^{6+}	mg/L	0.004	0.080	0.015	0.005	0.020	83.5	11.0	0	5.5	0

the groundwater in the area is weakly alkaline. The Chinese groundwater quality standards classify groundwater quality into five classes, and the upper limit of class III represents the guideline values for domestic purpose. In this study, 87.7% of groundwater samples in this study area show TDS less than 1 g/L, indicating freshwater, and 10.9% of the samples are brackish water with TDS ranging within 1–2 g/L. High TDS groundwater is represented with high SO_4^{2-} and Na^+ contents, indicating strong evaporative enrichments and water–rock interactions in the area. The Fe and Mn contents in some groundwater samples exceeded the standard limit for class III, indicating that the groundwater in some local areas might be in a reduction environment, which can also be evidenced by very low ORP values in some areas. Guanzhong Plain has developed agriculture. The application of nitrogen fertilizer has been increasing year after year to increase agricultural production, which has increased surface nitrogen pollution and exacerbated nitrate pollution in groundwater (Zhang et al. 2019a, b). Soluble nitrates leached from the use of fertilizers during agricultural activities will migrate in the aquifer with groundwater flow, expanding nitrate pollutions in groundwater (Li et al. 2014b). In this study, high nitrate concentrations were detected in 32.8% of groundwater samples, indicating that groundwater quality is strongly influenced by agricultural activities.

The dominant ions determine the type of groundwater. According to the average values, the dominance of cations in groundwater is $Ca^{2+} > Mg^{2+} > Na^+ > K^+$, while the dominance of anions is $HCO_3^- > SO_4^{2-} > Cl^-$. The content of Ca^{2+} in groundwater ranges from 30.4 to 220 mg/L. Similarly, HCO_3^- is the main anion in groundwater with an average content of 289.16 mg/L. Thus, the Piper diagram (Fig. 2) suggests that the HCO_3-Ca·Mg type is the dominant hydrogeochemical type, indicating that shallow groundwater in the area is dominated by fresh water which are typical hydrochemical characteristic of groundwater in recharge zones (Wang et al. 2022a). In addition, the SO_4·Cl-Ca·Mg

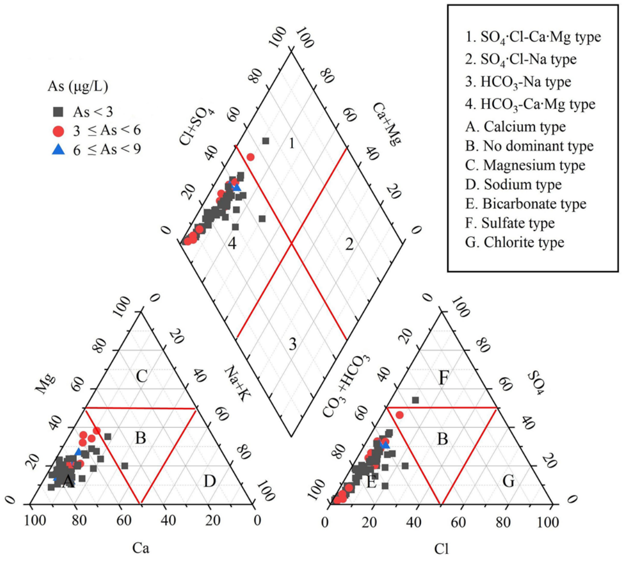


Fig. 2 Piper diagram of groundwater samples

type occurs in some areas of the region, suggesting the secondary effects of evaporation and human activities.

Concentration and Enrichment of Arsenic in Groundwater

The basic statistical analysis of arsenic concentrations in shallow groundwater in the study area showed that the concentrations of arsenic in groundwater ranged from 1.46 to 8.69 μg/L with a mean value of 2.66 μg/L, a median value of 2.29 μg/L, and a standard deviation of 1.24. According to the Chinese groundwater quality standards (General Administration of Quality Supervision, Inspection and Quarantine of the P. R. China and Standardization Administration of the P. R. China 2017), the concentration of arsenic in groundwater is within the groundwater quality standard limit for grade III. The World Health Organization also recommended guideline value of arsenic concentration in drinking water is 10 μg/L. In this research, the arsenic concentration in the groundwater samples is below this limit. However, arsenic is easy to accumulate and difficult to decompose in soil and plants, and can enter human body through food chain, which is harmful to human health (Ivy et al. 2022). Previous studies have shown that the arsenic content in drinking water in the Qinling area in southern Xi'an and eastern Xi'an is low, while the arsenic content in drinking water in the western Xi'an such as in the Huyi District (as high as 47 μg/L) is distinctly higher than in other areas, indicating a potential cancer risk to human health (Gao et al. 2022).

To obtain the spatial distribution characteristics of arsenic in groundwater in the study area, ordinary kriging interpolation technique was used for spatial interpolation, and the Golden Software Surfer 13 was used for the preparation of spatial distribution map. From Fig. 3, it can be seen that the content of arsenic in groundwater in Zhouzhi and Mei counties is low, while the content of arsenic in groundwater in the area around the Huyi District is significantly higher than that in the other areas. Researchers have shown that minerals associated with hydrothermal deposits, such as arsenopyrite (FeAsS) and fluorspar (CaF_2), are important sources of arsenic (Shahid et al. 2018a, b). Water–rock interactions between geothermal water and the hydrothermal deposits can produce dissolution of these minerals (Alarcon-Herrera et al. 2013), and it leads to high concentrations of arsenic in groundwater. There is a wide distribution of geothermal water in Xi'an, the region's active faults and widely distributed fractures provide convenient channels for the migration of arsenic in geothermal water to shallow groundwater. Therefore, the high concentration of arsenic found in shallow groundwater in the area can be partially explained by the upward movement of geothermal water and confined groundwater (Gao et al. 2020b).

The Pearson correlation matrix was used to further understand the correlation between arsenic and other physicochemical parameters, and the results are presented in Fig. 4. From Fig. 4, it can be seen that arsenic in groundwater was negatively correlated with ORP ($r = -0.455$) and was positively correlated with pH ($r = 0.417$), which indicated that

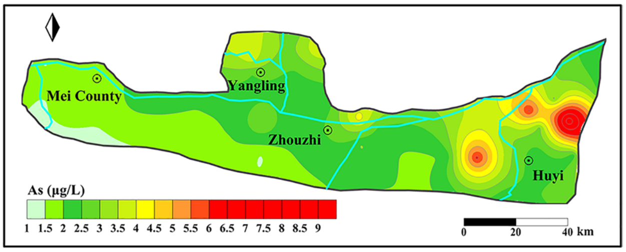
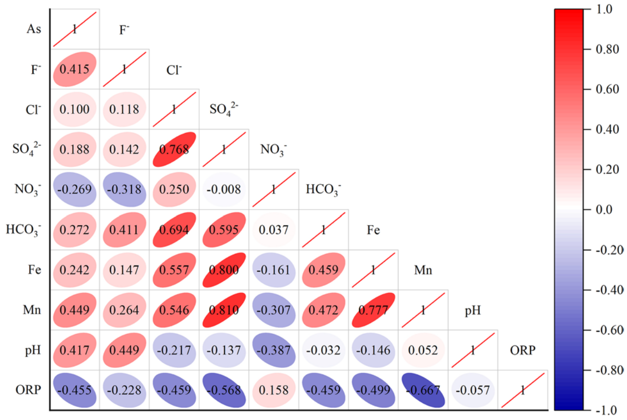


Fig. 3 Spatial distribution of As in groundwater



	As	F⁻	Cl⁻	SO_4^{2-}	NO_3^-	HCO_3^-	Fe	Mn	pH	ORP
As	1									
F⁻	0.415	1								
Cl⁻	0.100	0.118	1							
SO_4^{2-}	0.188	0.142	0.768	1						
NO_3^-	-0.269	-0.318	0.250	-0.008	1					
HCO_3^-	0.272	0.411	0.694	0.595	0.037	1				
Fe	0.242	0.147	0.557	0.800	-0.161	0.459	1			
Mn	0.449	0.264	0.546	0.810	-0.307	0.472	0.777	1		
pH	0.417	0.449	-0.217	-0.137	-0.387	-0.032	-0.146	0.052	1	
ORP	-0.455	-0.228	-0.459	-0.568	0.158	-0.459	-0.499	-0.667	-0.057	1

Fig. 4 Main existing chemical species of As and their percentage

alkaline reduction environment favors arsenic enrichment in the study area. Arsenic in groundwater can be very easily adsorbed by some positively charged minerals in the aqueous media, such as iron, aluminum oxides, hydrous aluminum, and hydrous iron ore. With the increase in pH, the positive charge of these colloidal and clay minerals gradually decreases, reducing the adsorption of arsenate and arsenite and making the concentration of arsenic in the surrounding water environment gradually increase. Changes in oxidation–reduction potential (ORP) affect the adsorption-resolution processes of arsenic in sediments, which in turn affect the concentration of arsenic in the water matrix. An aqueous environment with high pH and low ORP promotes the desorption of arsenic from sediments into groundwater and enhances its continuous accumulation in it (Gillispie et al. 2019). Many studies around the world have shown that arsenic in groundwater has a very intimate relationship with Fe and Mn (Haque and Johannesson 2006; Willis et al. 2011). In a reducing environment, the reductive dissolution of Fe/Mn oxide minerals is thought to be the main cause of arsenic enrichment in groundwater (Islam et al. 2004). In aqueous media, Fe/Mn oxide minerals are the main carriers of arsenic in groundwater system, as confirmed by the correlation of arsenic with Fe ($r=0.242$) and Mn ($r=0.449$) in Table 4. Arsenic was also positively correlated with HCO_3^- ($r=0.272$), which is the main anion in the groundwater of the study area with a concentration ranging from 125 to 642 mg/L (Table 3). High concentration of HCO_3^- in groundwater is usually associated with high pH values which would further promote the desorption of arsenic.

Occurrence Species of Arsenic

Studies on arsenic in groundwater have mainly concentrated on the total arsenic concentration which can be helpful to make a simple judgment on the pollution status of water bodies. However, total arsenic concentration cannot accurately analyze the biological effectiveness of arsenic. The toxicity of arsenic in water varies with its chemical valences, and the toxicity of arsenite (As(III)) is higher than that of arsenate (As(V)) (Ferguson and Gavis 1972; Guo et al. 2007). Therefore, to fully understand the biogeochemical cycling process, the chemical form of arsenic should be further explored. In this research, we adopted the PHREEQC model to calculate the different chemical species of arsenic, and the content of each chemical form of arsenic is listed as a percentage in this paper, and the results are shown in Fig. 5.

Table 4 Results of parameter sensitivity analysis

Random variables	Sensitivity of carcinogenic risk parameters (%)		Sensitivity of non-carcinogenic risk parameters (%)	
	Adults	Children	Adults	Children
Concentration of As in groundwater	72.6	72.4	72.5	72.4
Annual exposure frequency (EF)	15.9	15.7	14.7	15.7
Daily intake (IR)	5.8	5.8	6.3	5.8
Body weight	−5.7	−6.1	−6.5	−6.1

According to the simulation results, the major form of arsenic in most of the groundwater was $HAsO_4^{2-}$ and $H_2AsO_4^-$. It can be seen from Fig. 4 that $HAsO_4^{2-}$ is absolutely dominant in most of the water samples, with its content ranging from 16.49 to 88.66%, and the content of $H_2AsO_4^-$ in most water samples ranged from 11.32 to 49.83%. However, the main species of arsenic at sampling points G1-26 and G1-28 are relatively special, which are dominated by H_3AsO_3, with its content accounting for 98.82% and 96.11%, respectively. There are some differences in the species of arsenic at point G1-27, where the content of H_3AsO_3 accounted for 51.04%, and $HAsO_4^{2-}$ accounted for 38.1%, followed by a small amount of $H_2AsO_4^-$ and $H_2AsO_3^-$. Sampling point G1-29 was dominated by $H_2AsO_4^-$ with a ratio of 70.49%, followed by $HAsO_4^{2-}$ accounting for 17.17% and H_3AsO_3 accounting for 12.33%.In addition, the total amount of H_3AsO_4, AsO_4^{3-}, AsO_3^{3-}, $HAsO_3^{2-}$, and $H_4AsO_3^+$ in groundwater accounted for only 0.002–1.18%, indicating that they are minimal chemical species of arsenic.

Numerous studies have shown that high pH environments are favorable for arsenic desorption from minerals. Iron hydroxide can adsorb a large amount of arsenic in groundwater in low pH environment but arsenic can be released into groundwater environment with the increase of pH (Pierce and Moore 1982). The pH values of groundwater in the

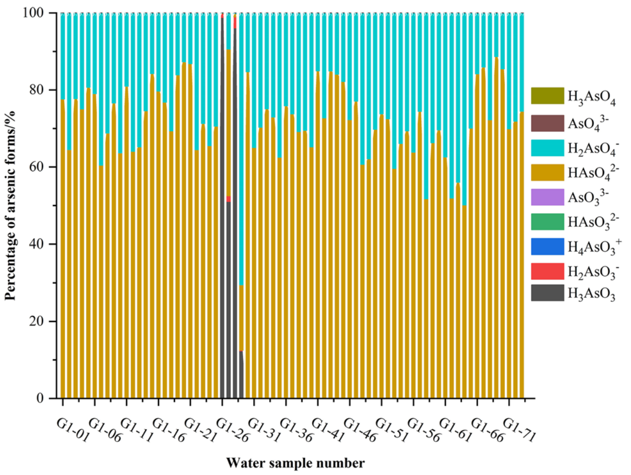


Fig. 5 Pearson correlation matrix of physicochemical parameters

study area are generally greater than 7.20, which indicates that it is a neutral environment in the research area, and in this environment, the clay minerals and iron hydroxide have a negative surface charge that exerts counterforce on arsenate and arsenite in the anionic form, while As(V) has a greater negative charge and desorbs more readily than As(III) (Jönsson and Sherman 2008), which may be one of the reasons for the predominance of As(V) in groundwater in the study area. Redox conditions also affect the valence state of arsenic, with arsenic compounds existing mainly as As(V) in an oxidation environment and As(III) in a reduction environment (Ding et al. 2022). Most of the water sample points have ORP values between 40 and 533 mV, indicating that they are in an oxidation environment, so the pentavalent $HAsO_4^{2-}$ and $H_2AsO_4^-$ are dominant, while the ORP values for samples G1-26 to G1-29 are negative, which indicates a reduction environment, thus making the trivalent H_3AsO_3 dominant at G1-26 to G1-29.

Two representative sampling points (G1-17 and G1-28) were selected to simulate the effects of acidity/alkalinity and redox conditions on the presence of arsenic using PHREEQC software, with G1-17 in an oxidation environment and G1-28 in a reduction environment. During the simulation, the pe values (pe is a parameter representing the oxidation–reduction conditions in the water solution) were first set unchanged while the pH values were changed to check the effects of pH on the presence of arsenic, and then pH was fixed and pe was changed to analyze the effects of oxidation–reduction conditions on the presence of arsenic. The simulation results are shown in Fig. 6. The simulation results show that in the oxidation environment when the water body is weakly acidic, arsenic in the water body mainly exists in the form of H_3AsO_3, and when the water body is near neutral, the main species of arsenic in the water body are H_3AsO_3, $H_2AsO_4^-$, and $HAsO_4^{2-}$. When the pH further increases to higher than 8.5, the main form of arsenic becomes $HAsO_4^{2-}$. However, under the reduction conditions, the main form of arsenic in the water is H_3AsO_3 in the weakly acidic environment, and when the water body is in a weakly alkaline environment, the main form of arsenic in the water is $HAsO_4^{2-}$. Since both sampling sites are in a weakly alkaline environment, their arsenic species shows the same trend with the change of pe. When the water body is in strong reduction condition, arsenic in the water body basically exists as As(III), mainly in the form of H_3AsO_3 and $H_2AsO_3^-$. As the pe value gradually increased, the contents of H_3AsO_3 and $H_2AsO_3^-$ gradually decreased, but the content of $HAsO_4^{2-}$ and $H_2AsO_4^-$ began to show an increasing trend. With the pe value further increased, $HAsO_4^{2-}$ and $H_2AsO_4^-$ dominated in the water body and their contents remained basically unchanged, while the content of other arsenic species kept almost zero. These simulation results have indicated that H_3AsO_3 is the primary chemical form of arsenic under the reduction conditions while arsenic exists mainly in the form of $HAsO_4^{2-}$ and $H_2AsO_4^-$ under the oxidation conditions. However, the contents of them will vary with the changes of pH in the water solution. These results can provide meaningful guidance for the treatment of high arsenic water.

Probabilistic Health Risk

The health risk of arsenic in groundwater in the study area to human through both oral and dermal exposure was assessed using a probabilistic approach with Monte Carlo simulations, and the results are shown in Fig. 7. The results show that the probability distribution for the health risk from human exposure to total arsenic follows a log-normal distribution, and the mean carcinogenic risk index for adults and children are 3.19×10^{-5} and 1.11×10^{-4}, respectively, and the mean values of HQ for adults and children are 0.18 and 0.41, respectively. Children, who generally have smaller weight than adults, are at higher risk than adults (Li et al. 2016). This is consistent with the results reported in many previous research papers (Guo et al. 2022; Wang et al. 2022b). The probabilities of the risk exceeding the threshold values of CR and HQ for children were 47.3% and 1.8%, respectively, indicating that arsenic in groundwater in the study area poses a high carcinogenic risk to children, while the non-carcinogenic risk for the children may be generally acceptable. Wei et al. (2022) conducted a study on arsenic enrichment in an area of the Yinchuan Basin, and assessed the health risk due to intake of high arsenic groundwater. They also obtained the same conclusion that children are at higher risk than adults, because children with lower body weight have more susceptible immune system than adults.

Sensitivity analysis can be helpful in determining the degree of response and sensitivity of multiple uncertainties to the target outcome (Gao et al. 2020a). A higher absolute value of sensitivity indicates a greater impact on target outcome. Table 4 shows the average sensitivity of health risks to uncertainty parameters in the following order: arsenic concentration > annual exposure frequency (EF) > human body weight > daily intake rate (IR), indicating the variable that contributes most to the health risk is the concentration of pollutants, followed by annual exposure frequency (EF), human body weight, and daily intake rate (IR). Therefore, it is concluded that enhanced control of arsenic concentration in groundwater in the study area can help to reduce significantly the carcinogenic and non-carcinogenic risks to humans. As such, treatment of arsenic and other contaminants becomes a necessity to ensure the safety of residents who consumes the groundwater in rural villages. At present, the groundwater pumped from private wells is not treated before consumed. It is

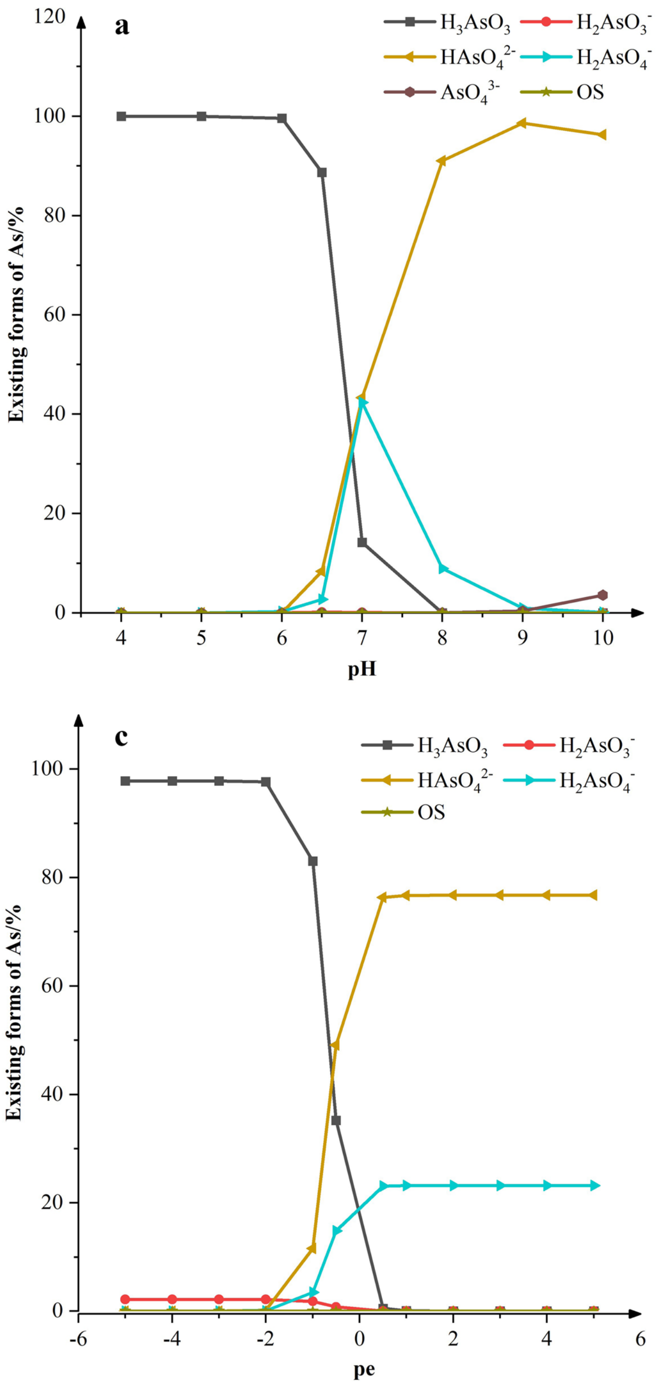


Fig. 6 The arsenic species changes with pH changes **a** G1-17 **b** G1-28 and pe changes **c** G1-17 **d** G1-28 (OS denotes other species)

recommended that local governments enhance centralized water supply in rural areas, otherwise, provide water treatment facilities to rural residents. In addition, children are at higher risk than adults, making it necessary for the governments to focus on reducing the health risks to children from arsenic in groundwater. It will be useful if the governments can supply bottled water to vulnerable age groups such as children. Therefore, finding alternative water sources for residents may become a top priority for the local government. Previous investigation indicated that the spring water in the Qinling mountainous region has very good quality, and it is highly suggested the spring water be gathered and supplied to rural residents.

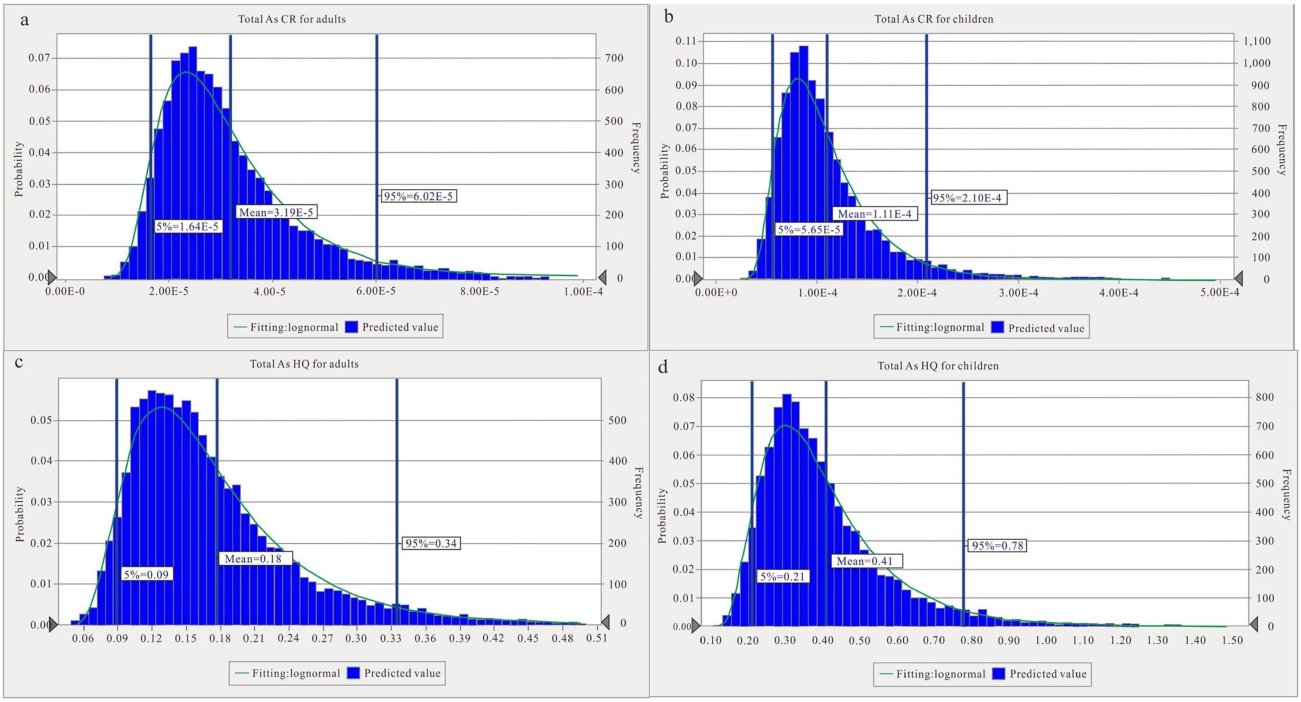


Fig. 7 Probabilistic health risk assessment results. CR of total As for **a** adults and **b** children, HQ of total As for **c** adults and **d** children

Limitations of this Study

Since Chinese drinking water quality evaluation standards do not require the analysis of As(III) and As(V), Chinese laboratories usually analyze only the total arsenic in water samples. The use of PHREEQC to model the species of arsenic present in water samples may have uncertainties. Therefore, the discussion on the species of arsenic has uncertainty, as the calculated species levels may be slightly different from the measured ones. However, the modeled species are still useful for understanding the speciation of arsenic. In addition, for the health risk assessment, since USEPA did not provide SF and RfD values for As(III), As(V), and organic species, this study did not consider and compare the health impacts of As(III) and As(V). Markley and Herbert (2009) estimated SF and RfD values of As(III) and As(V) in the previous studies. However, the derivation of these values based on cytotoxicity experiments is largely irrelevant to human external does, and the rapid interconversion of As(V) to As(III) in the human GIO system before it is absorbed may produce uncertainty to the assessment results. Therefore, future research is needed to determine the suitable parameter values for gaining more insights into the health impacts of As(III) and As(V) on human health.

Conclusions

In this study, the distribution and enrichment of arsenic in the groundwater in the typical rural areas along the northern foot of the Qinling Mountains were investigated. The different occurrence species of arsenic were calculated using PHREEQC, and the carcinogenic and non-carcinogenic risks caused by total arsenic were assessed using probabilistic models. The main conclusions are as follows:

(1) The concentration of arsenic in groundwater ranged from 1.46 to 8.69 μg/L in the studied area. The content of arsenic in groundwater in the area of Huyi District of Xi'an City is significantly higher than that in other areas.

(2) Based on the results of the PHREEQC simulation, the main species of arsenic in most groundwater in the study area are $HAsO_4^{2-}$ and $H_2AsO_4^{-}$, except some local samples with H_3AsO_3 as the main chemical form of arsenic followed by H_3AsO_4, AsO_4^{3-}, AsO_3^{3-}, $HAsO_3^{2-}$, and $H_4AsO_3^{+}$ which exist in only a relatively small proportion.

(3) The simulation results show that when the water is in a weakly acidic environment, arsenic mainly exists as H_3AsO_3; when the water is in a weakly alkaline envi-

ronment, the main form of arsenic is $HAsO_4^{2-}$. When the water body is under a reduction condition, the main form of arsenic is H_3AsO_3, followed by a small amount of $H_2AsO_3^-$, but when the water body is under oxidation, $HAsO_4^{2-}$ and $H_2AsO_4^-$ dominate in the water solution.

(4) The mean carcinogenic risk index for adults and children are 3.19×10^{-5} and 1.11×10^{-4}, respectively, and the mean values of HQ for adults and children are 0.18 and 0.41, respectively. This indicates that children are at higher risk due to exposure to arsenic in groundwater. The probability of CR and HQ exceeding the threshold value for children is 47.3% and 1.8%, respectively, indicating that arsenic in groundwater in the study area poses a high carcinogenic risk to children. Enhancing centralized water supply in which water will be treated before supplied and finding alternative water sources are suggested as good measures to reduce the health risk in rural areas.

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Author Contributions Q Du conducted the data analyses, conceptualized the core idea, conducted the simulation, and wrote the draft of the manuscript. J Wu refined the idea, wrote and edited the several versions of the manuscript, and supervised the entire research. F Xu, Y Yang, and F Li participated in the field work and wrote the draft. All authors approved the final version of the manuscript.

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Data Availability All the samples were collected by the authors' research team, and the raw data may be provided upon reasonable request.

Declarations

Conflict of interest The authors declare no conflict of interest.

References

Alarcon-Herrera MT, Bundschuh J, Nath B, Nicolli HB, Gutierrez M, Reyes-Gomez VM, Nunez D, Martin-Dominguez IR, Sracek O (2013) Co-occurrence of arsenic and fluoride in groundwater of semi-arid regions in Latin America: genesis, mobility and remediation. J Hazard Mater 262:960–969. https://doi.org/10.1016/j.jhazmat.2012.08.005

Alcaine AA, Schulz C, Bundschuh J, Jacks G, Thunvik R, Gustafsson JP, Morth CM, Sracek O, Ahmad A, Bhattacharya P (2020) Hydrogeochemical controls on the mobility of arsenic, fluoride and other geogenic co-contaminants in the shallow aquifers of northeastern La Pampa Province in Argentina. Sci Total Environ 715:136671. https://doi.org/10.1016/j.scitotenv.2020.136671

Bhowmick S, Pramanik S, Singh P, Mondal P, Chatterjee D, Nriagu J (2018) Arsenic in groundwater of West Bengal, India: a review of human health risks and assessment of possible intervention options. Sci Total Environ 612:148–169. https://doi.org/10.1016/j.scitotenv.2017.08.216

Bundschuh J, Maity JP (2015) Geothermal arsenic: occurrence, mobility and environmental implications. Renew Sustain Energy Rev 42:1214–1222. https://doi.org/10.1016/j.rser.2014.10.092

Cao Q, Yang L, Ren W, Yan R, Wang Y, Liang C (2021) Environmental geochemical maps of harmful trace elements in Chinese coalfields. Sci Total Environ 799:149475. https://doi.org/10.1016/j.scitotenv.2021.149475

Cao W, Gao Z, Guo H, Pan D, Qiao W, Wang S, Ren Y, Li Z (2022) Increases in groundwater arsenic concentrations and risk under decadal groundwater withdrawal in the lower reaches of the Yellow River basin, Henan Province, China. Environ Pollut 296:118741. https://doi.org/10.1016/j.envpol.2021.118741

Carraro A, Fabbri P, Giaretta A, Peruzzo L, Tateo F, Tellini F (2015) Effects of redox conditions on the control of arsenic mobility in shallow alluvial aquifers on the Venetian Plain (Italy). Sci Total Environ 532:581–594. https://doi.org/10.1016/j.scitotenv.2015.06.003

Chakraborty M, Mukherjee A, Ahmed KM (2015) A review of groundwater arsenic in the Bengal Basin, Bangladesh and India: from source to sink. Curr Pollut Rep 1:220–247. https://doi.org/10.1007/s40726-015-0022-0

Chakraborty M, Mishra AK, Mukherjee A (2022) Influence of hydrogeochemical reactions along flow paths on contrasting groundwater arsenic and manganese distribution and dynamics across the Ganges River. Chemosphere 287(2):132144. https://doi.org/10.1016/j.chemosphere.2021.132144

Chang F, Lei P, Meng Z, Zheng J, Zhang T (2019) Monitoring of toxicological indicators of rural drinking water in Shaanxi province from 2016 to 2018. Inst Health 48:6 (**in Chinese**)

Ding S, Wang Y, Yang M, Shi R, Ma T, Cui G, Li X (2022) Distribution and speciation of arsenic in seasonally stratified reservoirs: implications for biotransformation mechanisms governing interannual variability. Sci Total Environ 806:150925. https://doi.org/10.1016/j.scitotenv.2021.150925

Ferguson JF, Gavis J (1972) A review of the Arsenic cycle in natural waters. Water Res 6:1256–1274. https://doi.org/10.1016/0043-1354(72)90052-8

Ganyaglo SY, Gibrilla A, Teye EM, Owusu-Ansah E, Tettey S, Diabene PY, Asimah S (2019) Groundwater fluoride contamination and probabilistic health risk assessment in fluoride endemic areas of the Upper East Region, Ghana. Chemosphere 233:862–872. https://doi.org/10.1016/j.chemosphere.2019.05.276

Gao Y, Qian H, Ren W, Wang H, Liu F, Yang F (2020a) Hydrogeochemical characterization and quality assessment of groundwater based on integrated-weight water quality index in a concentrated urban area. J Clean Prod 260:121006. https://doi.org/10.1016/j.jclepro.2020.121006

Gao Y, Qian H, Wang H, Chen J, Ren W, Yang F (2020b) Assessment of background levels and pollution sources for arsenic and fluoride in the phreatic and confined groundwater of Xi'an city, Shaanxi, China. Environ Sci Pollut Res 27:34702–34714. https://doi.org/10.1007/s11356-019-06791-7

Gao Y, Qian H, Zhou Y, Chen J, Wang H, Ren W, Qu W (2022) Cumulative health risk assessment of multiple chemicals in groundwater based on deterministic and Monte Carlo models in a large semi-arid basin. J Clean Prod 352:131567. https://doi.org/10.1016/j.jclepro.2022.131567

General Administration of Quality Supervision, Inspection and Quarantine of the P. R. China, Standardization Administration of the P. R. China (2017) Standard for groundwater quality (GB/T 14848–2017). China Standards Press, Beijing (**in Chinese**)

Gillispie EC, Matteson AR, Duckworth OW, Neumann RB, Phen N, Polizzotto ML (2019) Chemical variability of sediment and groundwater in a Pleistocene aquifer of Cambodia: implications for arsenic pollution potential. Geochim Cosmochim Acta 245:441–458. https://doi.org/10.1016/j.gca.201811.008

Gong G, Mattevada S, O'Bryant SE (2014) Comparison of the accuracy of kriging and IDW interpolations in estimating groundwater arsenic concentrations in Texas. Environ Res 130:59–69. https://doi.org/10.1016/j.envres.2013.12.005

Guo H, Yang S, Shen Z (2007) High arsenic groundwater in the world: overview and research perspectives. Adv Earth Sci 154:1109–1117 (**in Chinese**)

Guo H, Yang S, Tang X, Li Y, Shen Z (2008) Groundwater geochemistry and its implications for arsenic mobilization in shallow aquifers of the Hetao Basin, Inner Mongolia. Sci Total Environ 393(1):131–144. https://doi.org/10.1016/j.scitotenv.2007.12.025

Guo H, Wen D, Liu Z, Jia Y, Guo Q (2014) A review of high arsenic groundwater in Mainland and Taiwan, China: distribution, characteristics and geochemical processes. Appl Geochem 41:196–217. https://doi.org/10.1016/j.apgeochem.2013.12.016

Guo Y, Li P, He X, Wang L (2022) Groundwater quality in and around a landfill in northwest China: characteristic pollutant identification, health risk assessment, and controlling factor analysis. Expo Health 14(4):885–901. https://doi.org/10.1007/s12403-022-00464-6

Haque S, Johannesson KH (2006) Arsenic concentrations and speciation along a groundwater flow path: the Carrizo Sand aquifer, Texas, USA. Chem Geol 228:57–71. https://doi.org/10.1016/j.chemgeo.2005.11.019

He J, Charlet L (2013) A review of arsenic presence in China drinking water. J Hydrol 492:79–88. https://doi.org/10.1016/j.jhydrol.2013.04.007

He XD, Li PY, Ji YJ, Wang YH, Su ZM, Vetrimurugan E (2020) Groundwater arsenic and fluoride and associated arsenicosis and fluorosis in China: occurrence, distribution and management. Expo Health 12:355–368. https://doi.org/10.1007/s12403-020-00347-8

Huq ME, Fahad S, Shao Z, Sarven MS, Khan IA, Alam M, Saeed M, Ullah H, Adnan M, Saud S, Cheng Q, Ali S, Wahid F, Zamin M, Raza MA, Saeed B, Riaz M, Khan WU (2020) Arsenic in a groundwater environment in Bangladesh: occurrence and mobilization. J Environ Manag 262:110318. https://doi.org/10.1016/j.jenvman.2020.110318

IARC (2011) Arsenic and inorganic arsenic compounds. Rep Carcinog 2:50–53

Islam FS, Gault AG, Boothman C, Polya DA, Charnock JM, Chatterjee D (2004) Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. Nature 430:68–71. https://doi.org/10.1038/nature02638

Islam MS, Mustafa RA, Phoungthong K, Islam AMT, Islam T, Choudhury TR, Kabir MH, Ali MM, Idris AM (2022) Arsenic in the foodstuffs: potential health appraisals in a developing country, Bangladesh. Environ Sci Pollut Res 58:698. https://doi.org/10.1007/s11356-022-24119-w

Ivy N, Mukherjee T, Bhattacharya S, Ghosh A, Sharma P (2022) Arsenic contamination in groundwater and food chain with mitigation options in Bengal delta with special reference to Bangladesh. Environ Geochem Health. https://doi.org/10.1007/s10653-022-01330-9

Jönsson J, Sherman D (2008) Sorption of As(III) and As(V) to siderite, green rust (fougerite) and magnetite: implications for arsenic release in anoxic groundwaters. Chem Geol 255:173–181. https://doi.org/10.1016/j.chemgeo.2008.06.036

Ke T, Zhang D, Guo H, Xiu W, Zhao Y (2022) Geogenic arsenic and arsenotrophic microbiome in groundwater from the Hetao Basin. Sci Total Environ 852:158549. https://doi.org/10.1016/j.scitotenv.2022.158549

Khan MU, Rai N, Sharma MK (2022) Geochemical behavior and fate of arsenic in middle Gangetic plain, Terai region of India, and its health risk quantification using Monte Carlo simulation and sensitivity analysis. Groundw Sustain Dev 19:100811. https://doi.org/10.1016/j.gsd.2022.100811

Kim SH, Kim K, Ko KS, Kim Y, Lee KS (2012) Co-contamination of arsenic and fluoride in the groundwater of unconsolidated aquifers under reducing environments. Chemosphere 87:851–856. https://doi.org/10.1016/j.chemosphere.2012.01.025

Kumar M, Das A, Das N, Goswami R, Singh UK (2016) Co-occurrence perspective of arsenic and fluoride in the groundwater of Diphu, Assam, Northeastern India. Chemosphere 150:227–238. https://doi.org/10.1016/j.chemosphere.2016.02.019

Li P, Qian H, Wu J, Chen J, Zhang Y, Zhang H (2014a) Occurrence and hydrogeochemistry of fluoride in alluvial aquifer of Weihe River, China. Environ Earth Sci 71:3133–3145. https://doi.org/10.1007/s12665-013-2691-6

Li P, Wu J, Qian H, Lyu X, Liu H (2014b) Origin and assessment of groundwater pollution and associated health risk: a case study in an industrial park, northwest China. Environ Geochem Health 36:693–712. https://doi.org/10.1007/s10653-013-9590-3

Li P, Li X, Meng X, Li M, Zhang Y (2016) Appraising groundwater quality and health risks from contamination in a semiarid region of northwest China. Expo Health 8:361–379. https://doi.org/10.1007/s12403-016-0205-y

Li P, He X, Guo W (2019a) Spatial groundwater quality and potential health risks due to nitrate ingestion through drinking water: a case study in Yan'an City on the Loess Plateau of northwest China. Hum Ecol Risk Assess 25:11–31. https://doi.org/10.1080/10807039.2018.1553612

Li P, He X, Li Y, Xiang G (2019b) Occurrence and health implication of fluoride in groundwater of loess aquifer in the Chinese Loess Plateau: a case study of Tongchuan, northwest China. Expo Health 11:95–107. https://doi.org/10.1007/s12403-018-0278-x

Li Z, Yang Q, Yang Y, Xie C, Ma H (2020) Hydrogeochemical controls on arsenic contamination potential and health threat in an intensive agricultural area, northern China. Environ Pollut 256:113455. https://doi.org/10.1016/j.envpol.2019.113455

Li C, Bundschuh J, Gao X, Li Y, Zhang X, Luo W, Pan Z (2022) Occurrence and behavior of arsenic in groundwater-aquifer system of irrigated areas. Sci Total Environ 838:155991. https://doi.org/10.1016/j.scitotenv.2022.155991

Li F, Wu J, Xu F, Yang Y, Du Q (2023) Determination of the spatial correlation characteristics for selected groundwater pollutants using the geographically weighted regression model: A case study in Weinan, Northwest China. Hum Ecol Risk Assess 29(2):471–493. https://doi.org/10.1080/10807039.2022.2124400

Liu L, Wu J, He S, Wang L (2022) Occurrence and distribution of groundwater fluoride and manganese in the Weining Plain (China) and their probabilistic health risk quantification. Expo Health 14:263–279. https://doi.org/10.1007/s12403-021-00434-4

Luo K, Zhang S, Tian Y, Gao X (2014) Arsenic distribution pattern in different sources of drinking water and their geological background in Guanzhong Basin, Shaanxi, China. Acta Geol Sin-Engl Ed 88:984–994. https://doi.org/10.1111/1755-6724.12251

Markley CT, Herbert BE (2009) Arsenic risk assessment: the importance of speciation in different hydrologic systems. Water Air Soil Pollut 204:385–398. https://doi.org/10.1007/s11270-009-0052-6

Meng X, Jing C, Korfiatis GP (2003) A review of redox transformation of arsenic in aquatic environments. Biogeochem Environ Important Trace Elem ACS Symp Ser 835:70–83. https://doi.org/10.1021/bk-2003-0835.ch006

Ministry of Environment Protection of the P.R. China (2014) Technical guidance for risk assessment of contaminated sites (HJ 25.3–2014). China Environment Science Press, Beijing (**in Chinese**)

Ministry of Environmental Protection of the P.R. China (2020) Technical specifications for environmental monitoring of groundwater (HJ/T 164–2020). China Environmental Science Press, Beijing (**in Chinese**)

Ministry of Land and Resources of the P. R. China (2006) The specification of testing quality management for geological laboratories (DZ/T 0130.6-2006). China Standards Press, Beijing (**in Chinese**)

Mondal D, Polya DA (2008) Rice is a major exposure route for arsenic in Chakdaha block, Nadia district, West Bengal, India: a probabilistic risk assessment. Appl Geochem 23(11):2987–2998. https://doi.org/10.1016/j.apgeochem.2008.06.025

Nottebaum V, Walk J, Knippertz M, Karthe D, Batbayar G, Potter S, Lehmkuhl F (2020) Arsenic distribution and pathway scenarios for sediments and water in a peri-urban Mongolian small-scale coal mining area (Nalaikh District, Ulaanbaatar). Environ Sci Pollut Res 27:5845–5863. https://doi.org/10.1007/s11356-019-07271-8

NRC (1999) Arsenic in drinking water. National Academy Press, Washington DC

Nsabimana A, Li P (2022) Hydrogeochemical characterization and appraisal of groundwater quality for industrial purpose using a novel industrial water quality index (IndWQI) in the Guanzhong Basin, China. Geochemistry 58:965. https://doi.org/10.1016/j.chemer.2022.125922

Nsabimana A, Li P, Wang Y, Alam SMK (2022) Variation and multi-time-series prediction of total hardness in groundwater of the Guanzhong Plain (China) using grey Markov model. Environ Monit Assess 194(12):899. https://doi.org/10.1007/s10661-022-10585-9

Nsabimana A, Wu J, Wu J, Xu F (2023) Forecasting groundwater quality using automatic exponential smoothing model (AESM) in Xianyang City, China. Hum Ecol Risk Assess 29(2):347–368. https://doi.org/10.1080/10807039.2022.2087176

Park J, Lee DY, Kim H, Woo NC (2023) Effects of dry and heavy rainfall periods on arsenic species and behaviour in the aquatic environment adjacent a mining area in South Korea. J Hazard Mater 441:129968. https://doi.org/10.1016/j.jhazmat.2022.129968

Pierce M, Moore C (1982) Adsorption of As(III) and As(V) on amorphous iron hydroxide. Water Res 16:1247–1253. https://doi.org/10.1016/0043-1354(82)90143-9

Qiao J, Zhu Y, Jia X, Shao M, Niu X, Liu J (2020) Distributions of arsenic and other heavy metals, and health risk assessments for groundwater in the Guanzhong Plain region of China. Environ Res 181:108957. https://doi.org/10.1016/j.envres.2019.108957

Rasheed H, Kay P, Slack R, Gong Y, Carter A (2017) Human exposure assessment of different arsenic species in household water sources in a high risk arsenic area. Sci Total Environ 584:631–641. https://doi.org/10.1016/j.scitotenv.2017.01.089

Ren X, Li P, He X, Su F, Elumalai V (2021) Hydrogeochemical processes affecting groundwater chemistry in the central part of the Guanzhong Basin, China. Arch Environ Contam Toxicol 80:74–91. https://doi.org/10.1007/s00244-020-00772-5

Rodriguez-Cantu LN, Martinez-Cinco MA, Balderas-Cortes JJ, Mondaca-Fernandez I, Navarro-Farfan MD, Meza-Montenegro MM (2022) Arsenic-contaminated drinking water and associated health risks in children from communities located in a geothermal site of Michoacan, Mexico: Monte Carlo probabilistic method. Hum Ecol Risk Assess 28:408–432. https://doi.org/10.1080/10807039.2022.2054771

Santha N, Sangkajan S, Saenton S (2022) Arsenic contamination in groundwater and potential health risk in western Lampang Basin, northern Thailand. Water 14(3):465. https://doi.org/10.3390/w14030465

Schreiber ME (2021) Arsenic in groundwater in the United States: research highlights since 2000, current concerns and next steps. Glob Groundw. https://doi.org/10.1016/B978-0-12-818172-0.00020-7

Shahid M, Khalid M, Dumat C, Khalid S, Niazi NK, Imran M, Bibi I, Ahmad I, Hammad HM, Tabassum RA (2018a) Arsenic level and risk assessment of groundwater in Vehari, Punjab Province, Pakistan. Expo Health 10:229–239. https://doi.org/10.1007/s12403-017-0257-7

Shahid M, Niazi NK, Dumat C, Naidu R, Khalid S, Rahman MM, Bibi I (2018b) A meta-analysis of the distribution, sources and health risks of arsenic-contaminated groundwater in Pakistan. Environ Pollut 242:307–319. https://doi.org/10.1016/j.envpol.2018.06.083

Shaji E, Santosh M, Sarath KV, Prakash P, Deepchand V, Divya BV (2021) Arsenic contamination of groundwater: A global synopsis with focus on the Indian Peninsula. Geosci Front 12:101079. https://doi.org/10.1016/j.gsf.2020.08.015

Sridharan M, Nathan DS (2018) Chemometric tool to study the mechanism of arsenic contamination in groundwater of Puducherry region, South East coast of India. Chemosphere 208:303–315. https://doi.org/10.1016/j.chemosphere.2018.05.083

Sun G (2004) Arsenic contamination and arsenicosis in China. Toxicol Appl Pharm 198(3):268–271. https://doi.org/10.1016/j.taap.2003.10.017

Tiankao W, Chotpantarat S (2018) Risk assessment of arsenic from contaminated soils to shallow groundwater in Ong Phra Sub-District, Suphan Buri Province, Thailand. J Hydrol-Reg Stud 19:80–96. https://doi.org/10.1016/j.ejrh.2018.08.001

USEPA (1989) Risk assessment guidance for superfund, volume I: human health evaluation manual (Part A). Office of Emergency and Remedial Response, Washington DC

USEPA (2004) Risk assessment guidance for superfund volume I: human health evaluation manual (Part E, supplemental guidance for dermal risk assessment). Washington DC

Villalba E, Tanjal C, Borzi G, Paez G, Carol E (2020) Geogenic arsenic contamination of wet-meadows associated with a geothermal system in an arid region and its relevance for drinking water. Sci Total Environ 720:137571. https://doi.org/10.1016/j.scitotenv.2020.137571

Wang Y, Li P (2022) Appraisal of shallow groundwater quality with human health risk assessment in different seasons in rural areas of the Guanzhong Plain (China). Environ Res 207:112210. https://doi.org/10.1016/j.envres.2021.112210

Wang L, Liu H, Xu X, Su M, Lin F, Ren L, Ren D, Fan X, Yu Z (1983) Investigation report on chronic endemic arsenic poisoning in Kuitun reclamation area, Xinjiang. Chin J Endemiol 2:71 (**in Chinese**)

Wang Z, Liu S, Chen X, Lin C (2008) Estimates of the exposed dermal surface area of Chinese in view of human health risk assessment. Northwest Geol 8(4):152–156 (**in Chinese**)

Wang J, Jin M, Jia B, Kang F (2022a) Numerical Investigation of Residence Time Distribution for the Characterization of Groundwater Flow System in Three Dimensions. J Earth Sci 33(6):1583–1600. https://doi.org/10.1007/s12583-022-1623-3

Wang L, Li P, Duan R, He X (2022b) Occurrence, controlling factors and health risks of Cr^{6+} in groundwater in the Guanzhong Basin of China. Expo Health 14(2):239–251. https://doi.org/10.1007/s12403-021-00410-y

Wang D, Li P, He X, He S (2023) Exploring the response of shallow groundwater to precipitation in the northern piedmont of the Qinling Mountains, China. Urban Clim 47:101379. https://doi.org/10.1016/j.uclim.2022.101379

Wei M, Wu J, Li W, Zhang Q, Su F, Wang Y (2022) Groundwater geochemistry and its impacts on groundwater arsenic enrichment, variation, and health risks in Yongning County, Yinchuan Plain of northwest China. Expo Health 14(2):219–238. https://doi.org/10.1007/s12403-021-00391-y

WHO (1993) Guidelines for drinking water quality, 2nd edn. World Health Organization, Geneva

Willis SS, Haque SE, Johannesson KH (2011) Arsenic and antimony in groundwater flow systems: a comparative study. Aquat Geochem 17:775–807. https://doi.org/10.1007/s10498-011-9131-6

Wu J, Sun Z (2016) Evaluation of shallow groundwater contamination and associated human health risk in an Alluvial Plain impacted by agricultural and industrial activities, Mid-west China. Expo Health 8:311–329. https://doi.org/10.1007/s12403-015-0170-x

Wu J, Zhang Y, Zhou H (2020) Groundwater chemistry and groundwater quality index incorporating health risk weighting in Dingbian County Ordos basin of northwest China. Geochemistry 80(4):125607. https://doi.org/10.1016/j.chemer.2020.125607

Xu D, Li P, Chen X, Yang S, Zhang P, Guo F (2023) Major ion hydrogeochemistry and health risk of groundwater nitrate in selected rural areas of the Guanzhong Basin, China. Hum Ecol Risk Assess. https://doi.org/10.1080/10807039.2022.2164246

Yang Y, Li P, Elumalai V, Ning J, Xu F, Mu D (2022) Groundwater quality assessment using EWQI with updated water quality classification criteria: a case study in and around Zhouzhi County, Guanzhong Basin (China). Expo Health. https://doi.org/10.1007/s12403-022-00526-9

Zhang J, Ma T, Feng L, Yan Y, Abass OK, Wang Z, Cai H (2017) Arsenic behavior in different biogeochemical zonations approximately along the groundwater flow path in Datong Basin, northern China. Sci Total Environ 584–585:458–468. https://doi.org/10.1016/j.scitotenv.2017.01.029

Zhang Y, Wu J, Xu B (2018) Human health risk assessment of groundwater nitrogen pollution in Jinghui canal irrigation area of the loess region, northwest China. Environ Earth Sci 77(7):273. https://doi.org/10.1007/s12665-018-7456-9

Zhang Q, Xu P, Qian H (2019a) Assessment of groundwater quality and human health risk (HHR) evaluation of nitrate in the Central-Western Guanzhong Basin, China. Int J Environ Res Public Health 16(21):4246. https://doi.org/10.3390/ijerph16214246

Zhang Y, Xu B, Guo Z, Han J, Li H, Jin L, Chen F, Xiong Y (2019b) Human health risk assessment of groundwater arsenic contamination in Jinghui irrigation district, China. J Environ Manag 237:163–169. https://doi.org/10.1016/j.jenvman.2019.02.067

Zhang Q, Li P, Lyu Q, Ren X, He S (2022a) Groundwater contamination risk assessment using a modified DRATICL model and pollution loading: a case study in the Guanzhong Basin of China. Chemosphere 291:132695. https://doi.org/10.1016/j.chemosphere.2021.132695

Zhang L, Li P, He X (2022b) Interactions between surface water and groundwater in selected tributaries of the Wei River (China) revealed by hydrochemistry and stable isotopes. Hum Ecol Risk Assess 28(1):79–99. https://doi.org/10.1080/10807039.2021.2016054

Zhou Y, Wu J, Gao X, Guo W, Chen W (2022) Hydrochemical background levels and threshold values of phreatic groundwater in the Greater Xi'an region, China: spatiotemporal distribution, influencing factors and implication to water quality management. Expo Health. https://doi.org/10.1007/s12403-022-00521-0

Zhou Y, Zhang C (2010) Shaanxi's per capita life expectancy ranked 21st in the country. Chinese Business Daily, Xi'an (**in Chinese**)

Zuo X (2011) Current status water intake of adults in four cities of China. Chinese Center for Disease Control and Prevention, Bejing (**in Chinese**)