



# Occurrence, Controlling Factors and Health Risks of Cr<sup>6+</sup> in Groundwater in the Guanzhong Basin of China

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## Abstract

Recently, high levels of Cr<sup>6+</sup> in groundwater have been found and are threatening public health in the Guanzhong Basin of China. For this reason, this study aims to specify the occurrence and spatial distribution of groundwater Cr<sup>6+</sup> and to analyze the favorable hydrogeochemical environment elevating its concentration in the Guanzhong Basin. The impacts of Cr<sup>6+</sup> on human health were also estimated based on the health risk assessment model recommended by the USEPA. Results show that 45.40% and 37.36% of the groundwater samples contain Cr<sup>6+</sup> concentration lower than 10 µg/L and ranging within 11–50 µg/L, respectively. And they are predominantly of HCO<sub>3</sub>-Ca and HCO<sub>3</sub>-Ca(Mg) water type. About 17.24% of the total water samples present Cr<sup>6+</sup> concentrations exceeding the acceptable limit for drinking purpose of 50 µg/L, and are mainly classified as HCO<sub>3</sub>-Na water type. Low Cr<sup>6+</sup> groundwater is mainly observed in the alluvial aquifer. Cr<sup>6+</sup> concentration in the samples from the loess aquifer is higher due to low groundwater velocity caused by the low permeability of loess, as verified by the relationship between Cr<sup>6+</sup> and major ions. The relationship between Cr<sup>6+</sup> and pH and molar ratio of Na<sup>+</sup>/(Na<sup>+</sup> + Ca<sup>2+</sup>) suggest that alkaline environment and cation exchange are beneficial to high concentration of Cr<sup>6+</sup> in groundwater. Industrial activities are also responsible for the elevation of Cr<sup>6+</sup> to some extent. Health risk assessment results show that the adults and children in the study area face higher carcinogenic risks than non-carcinogenic risk induced by Cr<sup>6+</sup>.

**Keywords** Groundwater pollution · Water quality · Hydrochemistry · Health risk · Guanzhong Basin

## Introduction

Groundwater is the primary source of drinking water for approximately 2 billion humans (Gleeson et al. 2010) and supports economic development and ecological environment (Li et al. 2021; Wang et al. 2020; Su et al. 2020). However, heavy metal pollution of groundwater and sediments is seriously affecting the sustainable development of groundwater resources (Kumar et al. 2020; Zhao et al. 2021; Li et al. 2015, 2016; Khan et al. 2020, 2021). Many studies have reported that Cr<sup>6+</sup> concentration in groundwater exceeded the acceptable limit of 50 µg/L recommended by the World

Health Organization for drinking purpose (Ball and Izbicki 2004; Bourotte et al. 2009; Coyte et al. 2020; He and Li 2020a; Kazakis et al. 2017; Manning et al. 2015; Mills et al. 2011; Vengosh et al. 2016). Chromium in natural groundwater systems is primarily present in two oxidation states, trivalent chromium (Cr<sup>3+</sup>) and hexavalent chromium (Cr<sup>6+</sup>). The speciation of chromium depends on pH and redox conditions of groundwater (Rajapaksha et al. 2013; Richard and Bourg 1991). Under alkaline and mild oxidization conditions, Cr<sup>6+</sup> will prevail in groundwater, while Cr<sup>3+</sup> will predominate under acidic and reduction conditions (Bourotte et al. 2009). Compared to Cr<sup>3+</sup>, Cr<sup>6+</sup> is more water soluble and is comparatively more mobile in groundwater (Coyte et al. 2020; Tseng et al. 2018). In addition, Cr<sup>3+</sup> is a micronutrient with a relatively low toxicity, but Cr<sup>6+</sup> is a known carcinogen. The intake of high levels of Cr<sup>6+</sup> can cause various types of cancer and DNA damage in humans, and this has been reported in a number of studies (Linos et al. 2011; Tseng et al. 2018).

Because of the high toxicity of Cr<sup>6+</sup>, the occurrence and sources of Cr<sup>6+</sup> as well as associated health risks in groundwater have attracted worldwide attention (He and Li 2020a).

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The occurrence of  $\text{Cr}^{6+}$  in groundwater largely depends on the geological background, especially those containing chromium such as ultramafic rocks and serpentinites of ophiolite complexes (Bourotte et al. 2009; Coyte et al. 2020; Equeenuddin and Pattnaik 2020; Kazakis et al. 2015; Lelli et al. 2014; Mills et al. 2011; Oze et al. 2007; Vengosh et al. 2016). The prevailing hydrogeological environment and geochemical processes may influence its concentration, such as pH (Oze et al. 2007), redox environment (Hausladen et al. 2018; Liang et al. 2021), vadose processes (Kazakis et al. 2015; Manning et al. 2015), and cation exchange (Bertolo et al. 2011; Mills et al. 2011). High levels of  $\text{Cr}^{6+}$  associated with natural sources are not common in a local region. Therefore,  $\text{Cr}^{6+}$  in groundwater can also be associated with various anthropogenic activities, such as coal combustion, fly ash deposits (Kazakis et al. 2017), paint manufacturing (Hausladen et al. 2018), mining activities (Kumari et al. 2017), leather tanning, phosphate fertilizer manufacturing (Molina et al. 2009; Vasileiou et al. 2019), as well as the overexploitation of groundwater (Gu et al. 2015; Testa et al. 2004).

The Guanzhong Basin lies in the middle of Shaanxi Province, being an important part of the Yellow River Basin. It belongs to the semi-humid and semiarid zone. It is also the most densely populated area and the most important agricultural area in northwest China (Deng et al. 2021; Ren et al. 2021). Limited surface water makes groundwater the main source of drinking water or other domestic purposes in this area, especially in rural and isolated urban areas. Groundwater polluted by nitrogen, fluoride and arsenic has been widely reported for a long time in the Guanzhong Basin and drawn a great deal of scholars' attention (Li et al. 2014; Luo et al. 2014; Wu and Sun 2016; Zhang et al. 2018, 2019; Zhu et al. 2006). However, high concentration of  $\text{Cr}^{6+}$  has also been found in the groundwater of Guanzhong Basin in recent years (Dong et al. 2018; Lei et al. 2019; Qiao et al. 2020). There are also many areas near the Guanzhong Basin that are polluted by  $\text{Cr}^{6+}$ , such as Yuncheng and Hejin in the west of Shanxi Province, Yan'an, Yulin in the northern of Shaanxi (Li 2006; Su et al. 2017; Tian and Wu 2019; Zhang 2012). According to the report, about 4% of the rural drinking water had concentrations of  $\text{Cr}^{6+}$  exceeding the acceptable level (50  $\mu\text{g}/\text{L}$ ) in the Guanzhong Basin, third only after fluoride and nitrogen, and even higher than arsenic (Chang et al. 2019). The rate of  $\text{Cr}^{6+}$  exceeding standard limit of groundwater (5.83%) was higher than that of surface water (0.27%) (Lei et al. 2019). Further, the studies on  $\text{Cr}^{6+}$  contamination of groundwater in the Guanzhong Basin are limited, and the distribution and occurrence of  $\text{Cr}^{6+}$  as well as associated influences on human health are not well understood. Accordingly, the main objectives of this study are (1) to delineate the occurrence and spatial distribution of groundwater  $\text{Cr}^{6+}$  in the Guanzhong Basin, (2) to analyze the

controlling factors influencing the concentration of groundwater  $\text{Cr}^{6+}$ , and (3) to estimate the health risks caused by  $\text{Cr}^{6+}$ . The results of this study may provide a scientific guidance for improving local groundwater quality to reduce the risk of  $\text{Cr}^{6+}$  exposure and support ecological protection and high-quality development in the Yellow River basin.

## Study Area

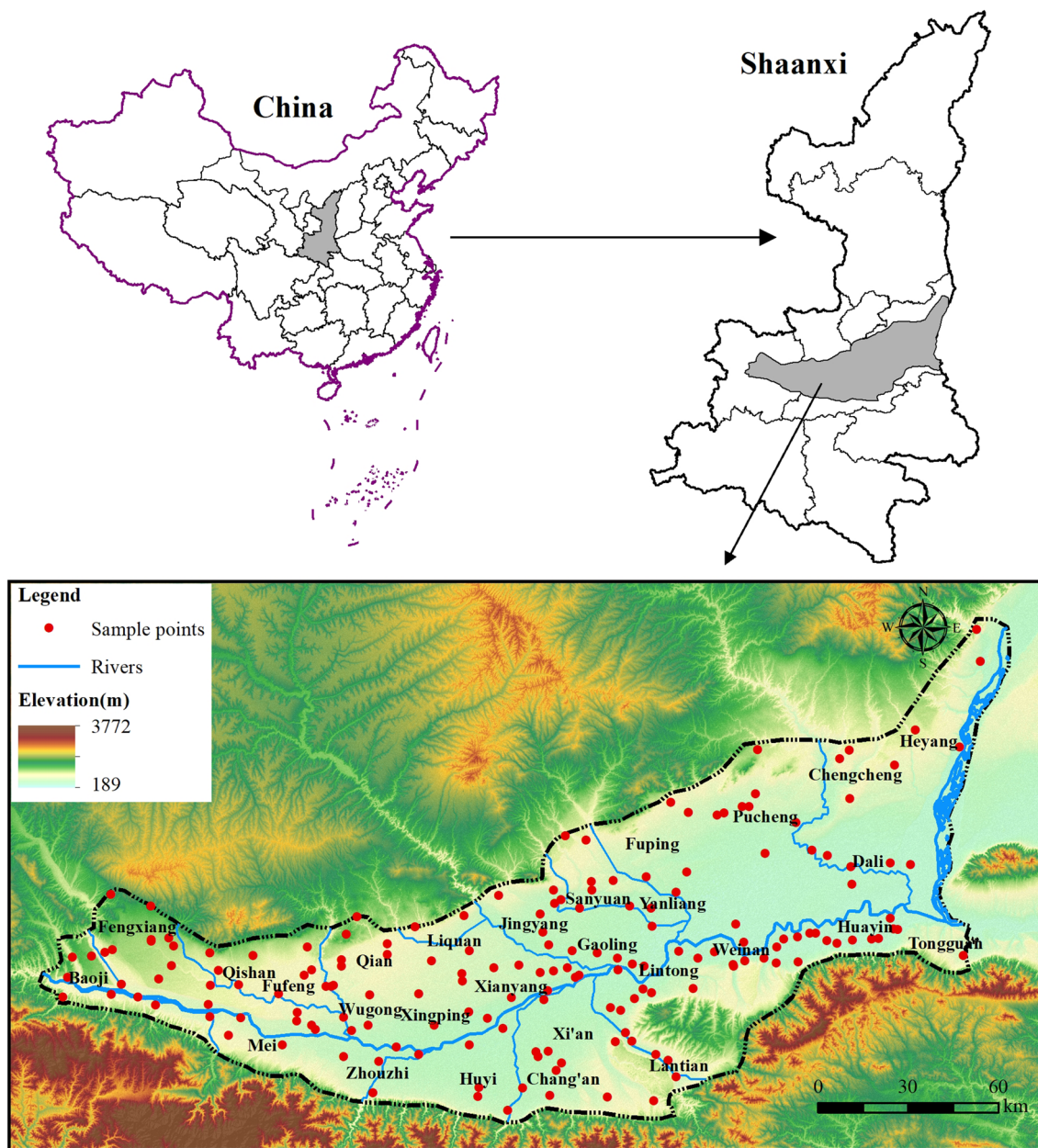
### Location and Geography

The Guanzhong Basin is located between longitude  $\text{E}107^{\circ}30'-110^{\circ}30'$  and latitude  $\text{N}34^{\circ}00'-35^{\circ}40'$ . The study area covers  $1.9 \times 10^{-4} \text{ km}^2$  and constitutes a basin surrounded on three sides by mountain ranges and open to the east. The Wei River flows across the basin from west to east and then empties into the Yellow River (Fig. 1). The occurrence of floods, loess accumulation and the Wei River flowing through this area supplies the geomorphology of the study area. From the north and south piedmont to the center of the basin, the landform types evolve stepwise from a piedmont pluvial plain into a loess tableland and a valley terrace. The general terrain of the study area is high in the west and low in the east, the altitude varies from 325 to 800 m. The climate in the study area is governed by the temperate semiarid and semi-humid monsoon climate characterized with a cold and dry winter and a hot and wet summer. The annual precipitation is 530–700 mm, where about 45% of the precipitation concentrates in July to September. The annual temperature and evaporation are 12–13.6 °C and 1000–1200 mm, respectively.

### Geological and Hydrological Settings

Geologically, the Guanzhong Basin is a Cenozoic fault basin formed by Himalayan movement. The basin subsided continuously and accepted deposition during the Late Eocene to Pliocene epochs, thereby accumulating very thick Tertiary fluvial–lacustrine facies in clastic rock. Deposition continued during the Quaternary, a thick layer of unconsolidated sediments overlay the Tertiary rocks. The Quaternary sediments of the basin are mainly lacustrine and alluvial deposits in the central part of the basin, and interbedded with alluvial, diluvial and loess deposits in the marginal areas.

The Guanzhong Basin is a relatively closed basin, which makes it an independent hydrogeological unit. Groundwater is widely distributed in the study area. According to geomorphology and hydrogeological conditions, aquifers in the Guanzhong Basin can be mainly divided into three types of which the first is the alluvial aquifer comprised by sand and sandy gravel. The second is the pluvial aquifer



**Fig. 1** Location of the study area showing the groundwater level and sampling sites

composed of sand, sandy gravel and boulder. The third group is the aeolian loess aquifer formed by loess layers (Fig. 3). The flow direction of groundwater is basically the same as the topography, that is, it flows from the southern and northern margins to the central areas of the basin, from the upper reaches to the lower reaches of the valley, and finally is discharged into rivers and valleys. The groundwater is mainly recharged by rainfall, river leakage, and irrigation infiltration. Groundwater discharge mainly occurs by artificial abstraction, evaporation, and discharging toward the river.

## Materials and Methods

### Datasets

For this study, the data of groundwater in the Guanzhong Basin were obtained from National Geological Archives of China (Li et al. 2018a). Sample collection and treatment methods can be seen in the paper published by Li et al. (2018a). Conductivity and pH were directly measured in the field using LOVIBOND multiparameter measuring instrument (SD150D) and geographical location names, latitude and longitude were recorded. Simultaneously, two 500 mL

water samples were collected and sealed in polyethylene plastic bottles and then sent to the Experimental Testing Center of Xi'an Institute of Geology and Mineral Resource for analysis of the other parameters. All analytical methods followed the national technical regulations (Ministry of Land and Resources of the P. R. China 2006). In addition, the groundwater hydrochemical data were validated by charge balance error percentage (CBE%). Finally, 174 groundwater samples with CBE% smaller than  $\pm 5\%$  were retained, and 13 hydrochemical parameters were selected for subsequent analysis of this study, including pH, TDS,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$  and  $\text{Cr}^{6+}$ .

### Human Health Risk Assessment

Human health risk assessment is an important methodology utilized to assess the probability of deleterious effects on human health to support water quality evaluation and management (Shukla and Saxena 2020). In this study, the non-carcinogenic and carcinogenic health risk of  $\text{Cr}^{6+}$  were estimated in two different age groups (adults and children) with the USEPA model (USEPA 1989). But only drinking water ingestion pathway was considered as the most remarkable source of exposure, because all the other exposure pathways such as inhalation and dermal absorption were negligible (Wu et al. 2019, 2020). Because potential health risk is posed only by one contaminant, the non-carcinogenic risk of  $\text{Cr}^{6+}$  through drinking water ingestion can be expressed by using the hazard quotient (HQ).  $\text{Cr}^{6+}$  is recognized as a Group 1 carcinogen by the WHO (World Health 2017), the carcinogenic risk (CR) of  $\text{Cr}^{6+}$  through drinking water ingestion can also be assessed. The computation can be conducted by the following equations (He et al. 2021; Wei et al. 2021; Li et al. 2019a, b).

$$\text{HQ} = \frac{\text{CDI}}{\text{RfD}} \quad (1)$$

$$\text{CR} = \text{CDI} \times \text{SF} \quad (2)$$

where RfD indicates the reference dosage for  $\text{Cr}^{6+}$  through drinking water ingestion pathway, and the value of RfD for

$\text{Cr}^{6+}$  is 0.003 mg/kg/day in this study. SF is the slope factor of  $\text{Cr}^{6+}$  (mg/kg/day), and the SF value of  $\text{Cr}^{6+}$  is set at 0.5 mg/kg/day. CDI denotes the chronic daily intake (mg/kg/day) and is determined with the following equation (He and Wu 2019; He et al. 2019; Ji et al. 2020).

$$\text{CDI} = \frac{C \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (3)$$

where  $C$  indicates the  $\text{Cr}^{6+}$  concentration in groundwater (mg/L); IR is ingestion rate of drinking water (in L/day); EF is the frequency of exposure (days/year); ED is the duration of exposure (years); BW is average body weight of a person (kg), and AT is average time for non-carcinogenic or carcinogenic effects (days). The reference values for computing CDI are determined by USEPA guidelines statistics data and adjusted according to the habits of local residents (Ministry of Environmental Protection of the P. R. China 2013). The values of these parameters are shown in Table 1.

## Results and Discussion

### $\text{Cr}^{6+}$ Concentration in Groundwater

The basic statistical analysis of groundwater  $\text{Cr}^{6+}$  concentrations was performed (Table 2). The analytical results indicate that the  $\text{Cr}^{6+}$  values range from 1 to 220  $\mu\text{g/L}$  with an average of 29  $\mu\text{g/L}$  and a median of 16  $\mu\text{g/L}$ . According to the groundwater quality standard of China (General Administration of Quality Supervision, Inspection and Quarantine of the P. R. China and Standardization Administration of the P. R. China 2017), the  $\text{Cr}^{6+}$  concentrations of groundwater in the study area can be divided into four intervals:  $\leq 10$ , 11–50, 50–100 and  $> 100$   $\mu\text{g/L}$ , respectively. Table 2 summarizes the percentages of groundwater samples classified

**Table 2** Statistics for percentages of groundwater samples at different  $\text{Cr}^{6+}$  concentration intervals

$\text{Cr}^{6+}$ concentration ( $\mu\text{g/L}$ )	$\leq 10$	11–50	50–100	$> 100$
Percentage (%)	45.40	37.36	9.77	7.47

**Table 1** Parameter values for health risk estimation

Parameter	Mean	Unit	Adults	Children
$C$	Concentration of $\text{Cr}^{6+}$ in water	mg/L	–	–
IR	Ingestion rate	L/day	1.9	1.1
EF	Exposure frequency	Days/year	365	365
ED	Exposure duration	Years	30	6
BW	Body weight	kg	62.5	25.8
AT	Non-carcinogenic average time	Days	$30 \times 365$	$6 \times 365$
	Carcinogenic average time	Days	$70 \times 365$	$70 \times 365$

by the four intervals. As shown in Table 2, the Cr<sup>6+</sup> concentrations of the groundwater samples are mainly in the range of ≤ 10 μg/L and 11–50 μg/L, accounting for 45.40% and 37.36% of the groundwater samples, respectively. In addition, about 17.24% of all groundwater samples measured for Cr<sup>6+</sup> (30 out of 174) exceeded the allowable limit for drinking purpose (50 μg/L), which indicates a potential cancer risk to human health.

### Hydrogeochemical Characteristics in Different Cr<sup>6+</sup> Concentration Intervals

The statistics for groundwater chemistry characteristics between different Cr<sup>6+</sup> concentration intervals are listed in Table 3. Groundwater samples with Cr<sup>6+</sup> concentration < 10 μg/L are characterized by highest mean concentrations of Ca<sup>2+</sup>, low levels of TDS and lowest mean concentrations of pH, Na<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and F<sup>-</sup>. Groundwater with Cr<sup>6+</sup> concentrations of 10–50 μg/L have lowest mean levels of TDS and SO<sub>4</sub><sup>2-</sup>, and the pH and other major ion (Na<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and F<sup>-</sup>) concentrations are a little higher than groundwater with Cr<sup>6+</sup> < 10 μg/L, but concentrations of Ca<sup>2+</sup> are lower by comparison. For Groundwater with Cr<sup>6+</sup> concentrations of 50–100 μg/L, their mean concentrations of TDS, Na<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and F<sup>-</sup> are elevated, and the Ca<sup>2+</sup> concentrations become even lower. Further, groundwater samples with Cr<sup>6+</sup> concentration > 100 μg/L have the lowest mean concentrations of Ca<sup>2+</sup> (mean 42.6 mg/L), and highest mean concentrations of TDS, Na<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>. These results indicate the occurrence of Cr<sup>6+</sup> is greatly related to the interaction between water and rock, because the concentration of major ions increases with the increase of Cr<sup>6+</sup> concentration interval except Ca<sup>2+</sup>.

Figure 2 plots the Piper diagram (He and Li 2020b) for the four Cr<sup>6+</sup> concentration intervals of the groundwater samples to study the hydrochemical types of groundwater. This figure indicates that the groundwater samples are predominantly of the HCO<sub>3</sub>-Ca(Mg) water types, and this agrees with the findings of Duan et al. (2011). It shows that carbonate dissolution is an important process regulating the major anions. The groundwater samples with Cr<sup>6+</sup> concentrations < 50 μg/L are clearly distinguished from those > 50 μg/L. Groundwater in Cr<sup>6+</sup> concentration intervals ≤ 10 μg/L and 11–50 μg/L

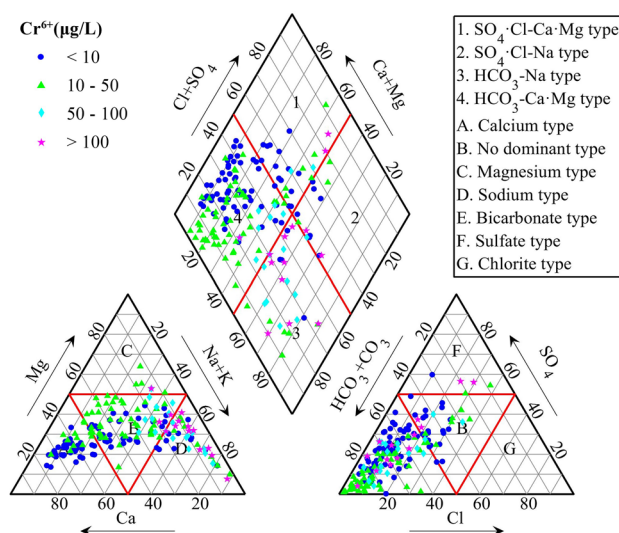


Fig. 2 Piper diagram showing the hydrochemical characteristics of different Cr<sup>6+</sup> concentration intervals

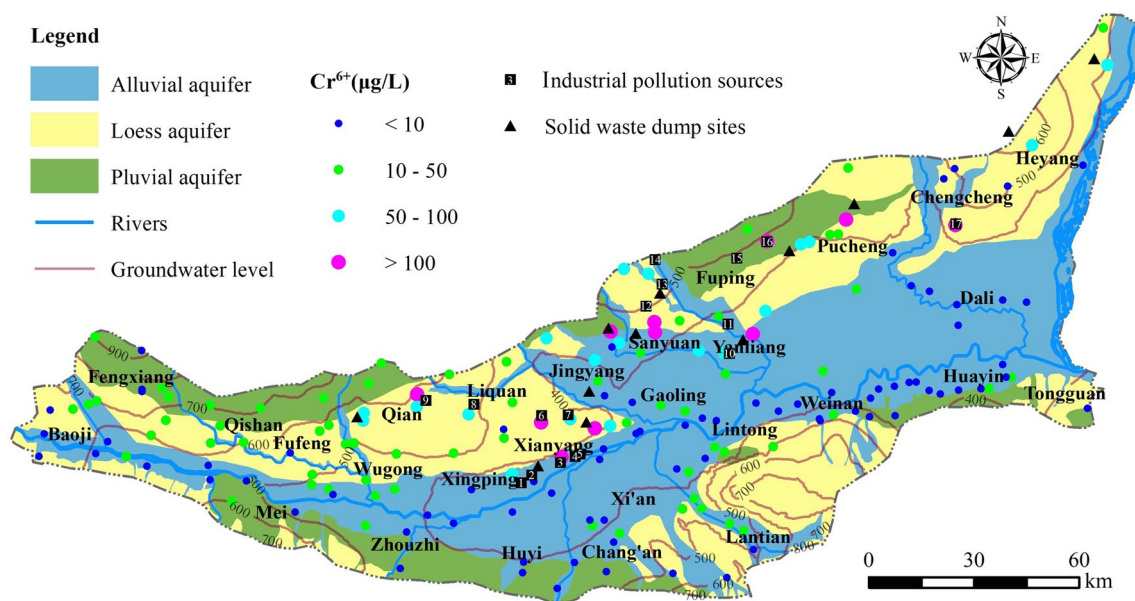
are mainly of HCO<sub>3</sub>-Ca and HCO<sub>3</sub>-Ca(Mg) type, and a portion of groundwater samples can be classified as HCO<sub>3</sub>-Na or SO<sub>4</sub>-Cl-Na types. Groundwater having Cr<sup>6+</sup> concentrations > 50 μg/L are classified as HCO<sub>3</sub>-Na type, and several samples are plotted in SO<sub>4</sub>-Cl-Na or SO<sub>4</sub>-Cl-Ca-Mg type zone. The observation of Piper diagram suggests that low concentrations of Cr<sup>6+</sup> are associated with high Ca<sup>2+</sup> and that high Cr<sup>6+</sup> samples are low Ca<sup>2+</sup> and high Na<sup>+</sup> water.

### Spatial Distribution of Cr<sup>6+</sup> in Groundwater

The spatial distribution of Cr<sup>6+</sup> is delineated in Fig. 3. As a whole, the concentration of groundwater Cr<sup>6+</sup> in the north of Weihe River is higher than that in the south of Weihe River. Groundwater Cr<sup>6+</sup> concentrations ≤ 10 μg/L are mainly found in the alluvial aquifer and pluvial aquifer occurring at the northern base of the Qinling Mountain. Most of the groundwater samples from the pluvial aquifer located in the north of the Wei River and most of the loess aquifer show that the Cr<sup>6+</sup> concentrations range from 11 to 50 μg/L. Zones with groundwater Cr<sup>6+</sup> concentrations > 50 μg/L are mainly distributed in the loess aquifer and a portion of alluvial

Table 3 Mean values of the physicochemical indices within different Cr<sup>6+</sup> concentration intervals

Cr <sup>6+</sup> concentration interval (μg/L)	pH	TDS mg/L	Na <sup>+</sup> mg/L	K <sup>+</sup> mg/L	Ca <sup>2+</sup> mg/L	Mg <sup>2+</sup> mg/L	Cl <sup>-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	HCO <sub>3</sub> <sup>-</sup> mg/L	CO <sub>3</sub> <sup>-</sup> mg/L	NO <sub>3</sub> <sup>-</sup> mg/L	F <sup>-</sup> mg/L
≤ 10	7.71	911.6	105.0	4.0	111.1	48.8	76.6	178.3	458.0	0.1	44.5	0.7
11–50	7.85	815.4	107.9	2.8	77.5	56.6	81.5	134.4	479.2	4.0	50.1	0.9
50–100	7.94	1110.4	202.3	1.1	47.1	71.8	110.5	187.6	599.2	1.3	76.7	1.4
> 100	7.94	1371.5	244.6	1.8	42.6	78.7	125.0	317.7	565.3	3.5	42.6	1.6



**Fig. 3** Spatial distributions of groundwater  $\text{Cr}^{6+}$ , overlying hydrogeological map

aquifer in the Yanliang district, Xianyang City, Qian, Jingyang, Sanyuan and Pucheng Counties, and these areas are high-risk zones to health issues due to high  $\text{Cr}^{6+}$  concentrations exceeding the limit for drinking. Previous studies have also revealed the occurrence of  $\text{Cr}^{6+}$  in both groundwater and surface water in the loess areas of China (He and Li 2020a; Xiao et al. 2019). Groundwater samples with  $\text{Cr}^{6+}$  concentration  $> 100 \mu\text{g/L}$  were concentrated in Xianyang City and Sanyuan County, which may induce a greater risk of disease associated with excessive  $\text{Cr}^{6+}$  concentrations. The above results indicate that the geological characteristics of loess may promote the occurrence of  $\text{Cr}^{6+}$ .

To understand how loess affects the concentration of  $\text{Cr}^{6+}$  in groundwater, total Cr in the soil of the Guanzhong Basin was measured in 2019. The spatial distribution of total Cr in the soil is generated. As shown in Fig. 4, the total Cr levels in the soil are higher in the south of the Weihe River Basin than in the north of the basin, and higher in the west than in the east of the basin, which is similar to continental-scale spatial distribution of chromium in catchment sediment/alluvial soil of China published by Yan et al. (2021). However, the total Cr distribution in soil is inconsistent with that of  $\text{Cr}^{6+}$  in groundwater in the Guanzhong Basin, because Cr is present in the loess in the form of  $\text{Cr}^{3+}$  instead of  $\text{Cr}^{6+}$  as revealed by the research of He and Li (2020a). This indicates that the total Cr in sediments does not have direct effect on the occurrence and distribution of  $\text{Cr}^{6+}$  in groundwater of the Guanzhong Plain. However, the loess provides the geogenic source of  $\text{Cr}^{3+}$  to form groundwater  $\text{Cr}^{6+}$ . Thus, it can be inferred that the high concentration of  $\text{Cr}^{6+}$  may be attributed to the low groundwater velocity

caused by the low permeability of loess. Lower groundwater seepage velocity can be associated with longer residence time of the groundwater, favoring the transform of  $\text{Cr}^{3+}$  in the loess into  $\text{Cr}^{6+}$  in groundwater. This is consistent with the previous result that the occurrence of  $\text{Cr}^{6+}$  is greatly related to water–rock interactions.

### Hydrogeochemical Factors Controlling $\text{Cr}^{6+}$ Concentrations

Hydrogeochemical processes are accountable for the occurrence of the  $\text{Cr}^{6+}$  in groundwater. The analysis of the relationship between  $\text{Cr}^{6+}$  and the other chemical components in groundwater is helpful for achieving a further understanding of the occurrence of groundwater  $\text{Cr}^{6+}$  in a study area (Fig. 5). As shown in Fig. 5a, there is weak linear relationship between groundwater  $\text{Cr}^{6+}$  and pH, but the higher concentrations of  $\text{Cr}^{6+}$  do tend to occur between about pH 7.7–8.5. This indicates that an alkaline environment is more conducive to  $\text{Cr}^{6+}$  occurrence in groundwater, because of stronger sorption and greater tendency toward reduction under neutral and acid environment (Bertolo et al. 2011; Coyte et al. 2020).

As shown in Fig. 5b, c, there are a positive correlation between  $\text{Cr}^{6+}$  and  $\text{Na}^+$ , and a negative relationship between  $\text{Cr}^{6+}$  and  $\text{Ca}^{2+}$  in groundwater, indicating that occurrence mechanism for high  $\text{Cr}^{6+}$  concentration is likely related to Ion exchange between  $\text{Ca}^{2+}$  and  $\text{Na}^+$  ions, which removed  $\text{Ca}^{2+}$  from groundwater by replacing with  $\text{Na}^+$  on the surfaces of the clay minerals. The exchange occurs particularly in the aquifer sediment matrixes consisting of fine particles

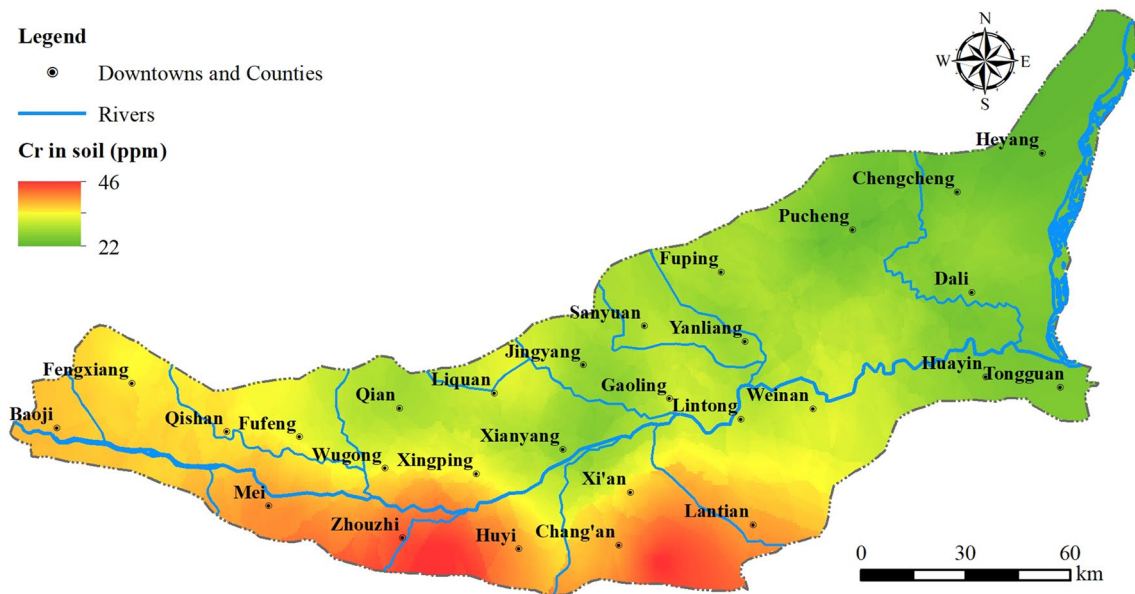


Fig. 4 Spatial distribution of Cr in the soil samples of the study area

like clay and silty clay. Bourotte et al. (2009) also found cation exchange between Ca<sup>2+</sup> and Na<sup>+</sup> may result in the desorption of Cr<sup>6+</sup> to the aquifer.

In this study, Chloro alkaline indices (CAI-1 and CAI-2) proposed by Schoeller was used to evaluate the process of cation exchange. CAI-1 and CAI-2 can be calculated as follows, where all ions are expressed in meq/L (Li et al. 2018b).

$$\text{CAI-1} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{\text{Cl}^-} \quad (4)$$

$$\text{CAI-2} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{\text{SO}_4^{2-} + \text{CO}_3^{2-} + \text{HCO}_3^- + \text{NO}_3^-} \quad (5)$$

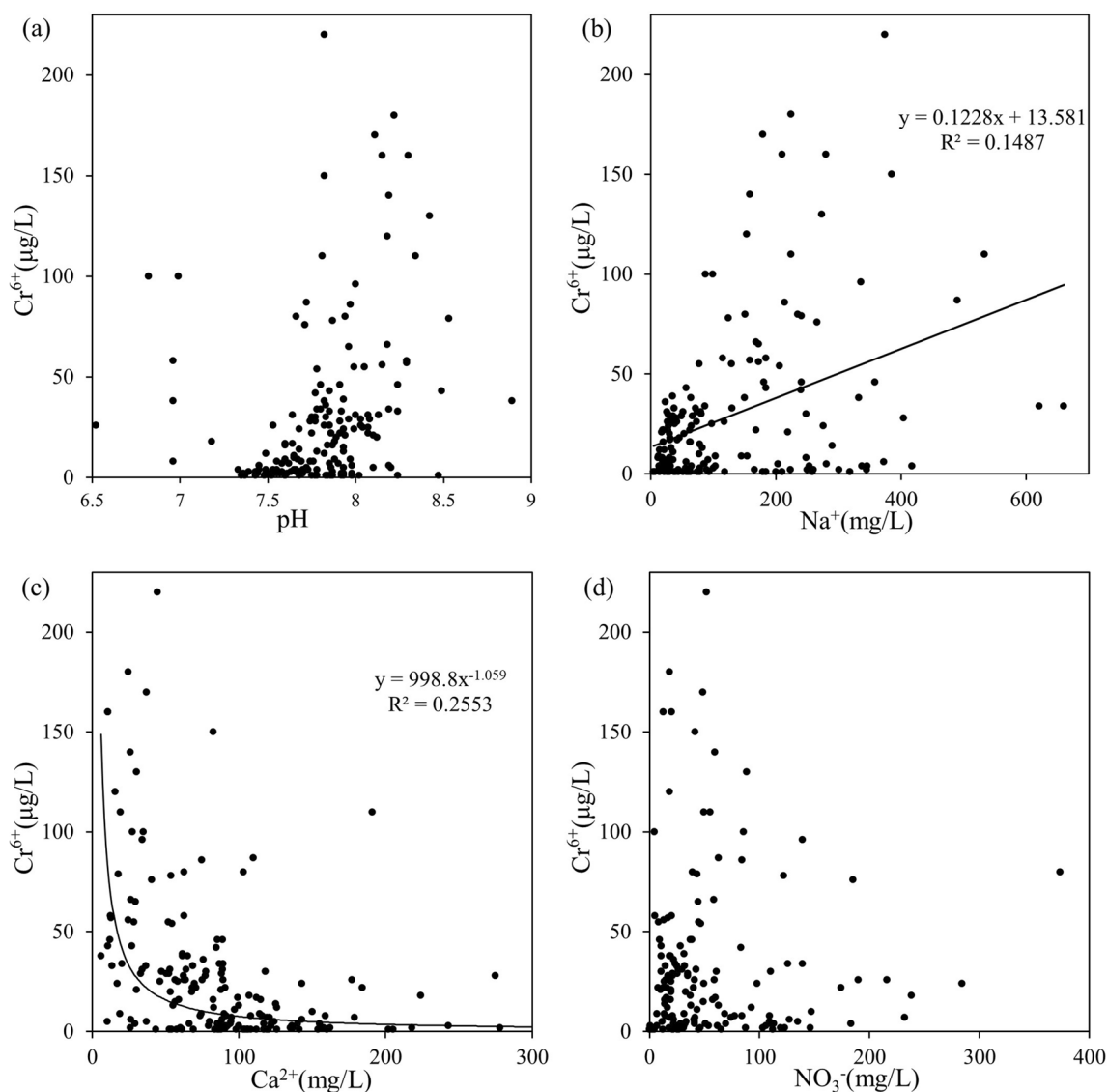
When CAI-1 and CAI-2 both have negative values, indicating that cation exchange processes occur between Ca<sup>2+</sup> in groundwater is exchanged for adsorbed Na<sup>+</sup> in sediment. However, if the indices were both positive, the exchange occurred in the reverse order. As shown in Fig. 6a, negative CAI-1 and CAI-2 values in most of the groundwater samples indicate that cation exchange of Na<sup>+</sup> in sediment against Ca<sup>2+</sup> in the groundwater may prevail across the entire basin. Meanwhile, the relationship between Cr<sup>6+</sup> concentration and the molar ratio of Na<sup>+</sup> to (Na<sup>+</sup> + Ca<sup>2+</sup>) is showed to signify the impact of cation exchange on Cr<sup>6+</sup> concentrations in the study area (Fig. 6b). Figure 6b indicates that the intensive cation exchange led to the molar ratio of Na<sup>+</sup> to (Na<sup>+</sup> + Ca<sup>2+</sup>) approaching to one and high Cr<sup>6+</sup> concentration. This is because cation exchange decreases the concentration of Ca<sup>2+</sup> and seems to driving the dissolution of carbonate minerals, increasing the pH and HCO<sub>3</sub><sup>-</sup> concentration. Further,

the increasing monovalent Na<sup>+</sup> concentrations compared to the divalent Ca<sup>2+</sup> concentrations can reduce the repulsive potential between the positive hydrous metal oxide surfaces and negative ions with the help of alkaline conditions, and thus promote the desorption of Cr<sup>6+</sup> anions (CrO<sub>4</sub><sup>2-</sup>) to the aquifer following the counterion effects (Liu et al. 2018; Zachara et al. 1987).

### Impacts of Human Activities on Cr<sup>6+</sup>

Human activities can affect the occurrence and distribution of Cr<sup>6+</sup>. Industrial emissions can affect the concentration of Cr<sup>6+</sup> in groundwater through leaching. As shown in Fig. 3, groundwater samples with high concentrations of Cr<sup>6+</sup> are accompanied by industrial pollution sources and solid waste dump sites. Furthermore, the information of industrial pollution sources listed in Table 4 shows that many industrial pollution sources, such as electroplating, printing and dyeing, fertilizer manufacturing and other enterprises, are widely distributed in the high Cr<sup>6+</sup> areas. These industrial pollution sources can discharge a large amount of chromium-containing wastes and/or wastewater to the environment, causing the elevation of Cr<sup>6+</sup> concentration in the surrounding groundwater. For example, Xianyang downtown has densely distributed industries, correspondingly groundwater is heavily polluted by Cr<sup>6+</sup> (Dong et al. 2018; Wang et al. 2012).

The use of fertilizer in agriculture may also be a potential factor affecting the concentration of Cr<sup>6+</sup> in groundwater, because phosphate fertilizer usually contains a certain amount of chromium, particularly in inferior phosphate fertilizer. In the Guanzhong Basin, the NO<sub>3</sub><sup>-</sup> concentration in



**Fig. 5** The relationship between concentrations of  $\text{Cr}^{6+}$  and pH (a),  $\text{Cr}^{6+}$  and  $\text{Na}^+$  (b),  $\text{Cr}^{6+}$  and  $\text{Ca}^{2+}$  (c),  $\text{Cr}^{6+}$  and  $\text{NO}_3^-$  (d)

groundwater ranges from 0.16 to 373.00 mg/L with an average of 49.57 mg/L, indicating that the agricultural activities affect the groundwater quality due to fertilizer as well as animal and human wastes (Duan et al. 2011). However,  $\text{Cr}^{6+}$  concentration in groundwater shows a poor correlation with  $\text{NO}_3^-$  (Fig. 5d), suggesting that input from agricultural activities do not affect the  $\text{Cr}^{6+}$  level in groundwater.

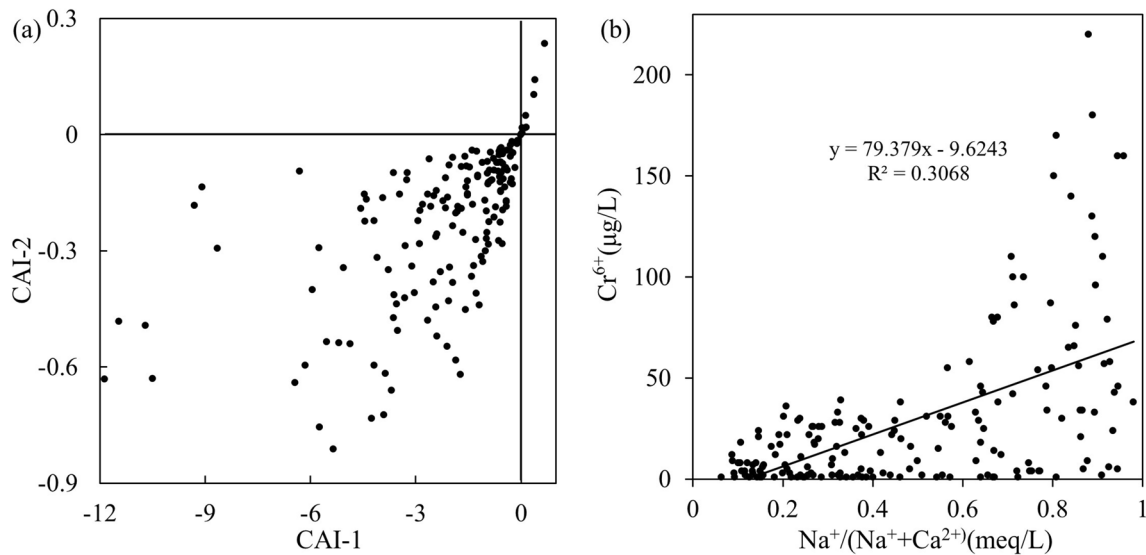
### Health Impacts of Groundwater $\text{Cr}^{6+}$

High  $\text{Cr}^{6+}$  level in groundwater may pose serious health hazards to local populace through multiple exposure pathways, especially for the drinking intake of untreated water. Therefore, the health risk assessment methodology was used to estimate the non-carcinogenic and carcinogenic health risks

to adults and children by  $\text{Cr}^{6+}$ . Table 5 presents the statistical results of the risk assessment to adults and children when they are exposed through drinking water intake.

For the non-carcinogenic risk, if  $\text{HQ} > 1$  is considered that there is a certain health risk. The values of HQ for adults range from 0.010 to 2.229 with an average value of 0.294, with 7.47% samples exceeding the acceptable limit value. However, the HQ values for children range from 0.014 to 3.127 with an average value of 0.413, about 12.07% of the total samples with the HQ values than 1. Above results indicate that non-carcinogenic health risk caused by  $\text{Cr}^{6+}$  is under the acceptable level through drinking water ingestion pathway in most of study area. Meanwhile, children are at higher non-carcinogenic risk than adults owing to lower body weight for children.





**Fig. 6** Plots of CAI-1 against CAI-2 (a), and Na<sup>+</sup>/(Na<sup>+</sup> + Ca<sup>2+</sup>) versus Cr<sup>6+</sup> (b)

**Table 4** List of industrial pollution source information

Number	Name of pollution source	Process that causes pollution
1	Xianyang Textile Industrial Park	Printing and dyeing, leather tanning
2	Shaanxi Xinyu Surface Engineering Co., Ltd	Electroplating
3	Xianyang Northwest Medical Instrument Co., Ltd	Electroplating
4	Xianyang Jihuaxin Sanzero Printing and Dyeing Co., Ltd	Printing and dyeing
5	Shaanxi xianyang chemical industry Co., Ltd	Chemical engineering
6	Liquan xinwei casting Co., Ltd	Electroplating
7	Xianyang baofeng biological fertilizer factory	Fertilizer manufacturing
8	Liquan Industrial Park	Electroplating, metal processing
9	Qianxian Industrial Park	Printing and dyeing, coating production
10	Xi'an Aircraft Industry Aluminium Co., Ltd	Electroplating
11	Yanliang Industrial Park	Electroplating, metal processing
12	Shaanxi White Deer Pharmaceutical Co., Ltd	pharmaceutical technique
13	Zhuangli Industrial Park	Metal processing, coal combustion
14	Shaanxi shaanjao chemical industry Co., Ltd	Coal combustion
15	Fuping Wofuda Biological Technology Co., Ltd	Fertilizer manufacturing
16	Lime/brick kiln	Coal combustion
17	Shaanxi Dongsheng Garment Co., Ltd	Printing and dyeing

**Table 5** Statistical results of health risk assessment

Age group	Non-carcinogenic risk (HQ)				Carcinogenic risk (CR)			
	Min	Max	Mean	Proportion of samples inducing risk	Min	Max	Mean	Proportion of samples inducing risk
Adults	0.010	2.229	0.294	7.47%	6.51E-06	1.43E-03	1.89E-04	50.57%
Children	0.014	3.127	0.413	12.07%	1.83E-06	4.02E-04	5.31E-05	16.67%

In terms of the carcinogenic risk, there are multiple standards for the acceptable levels of cancer risk, such as  $10^{-4}$  in Netherlands,  $10^{-5}$  in Canada and New Zealand, and  $10^{-6}$  in America and Australia. In this study, value of carcinogenic risk above  $10^{-4}$  is considered as unacceptable. The values of carcinogenic risk range from  $6.51\text{E}-06$  to  $1.43\text{E}-03$  with a mean value of  $1.89\text{E}-04$  for adults and vary from  $1.83\text{E}-06$  to  $4.02\text{E}-04$  with a mean value of  $5.31\text{E}-05$  for children. 50.57% of the total samples for adults and 16.67% of the sample for children exceed the acceptable limit of the carcinogenic risk ( $10^{-4}$ ). It is obvious that the carcinogenic risk of  $\text{Cr}^{6+}$  has a higher impact than non-carcinogenic risk for adults and children. However, in contrast to the non-carcinogenic risk, the carcinogenic risk of  $\text{Cr}^{6+}$  for adults is significantly higher than that for children, because the longer exposure duration leads to the accumulation of  $\text{Cr}^{6+}$  in the body. The study results indicate that groundwater treatment is necessary to reduce the  $\text{Cr}^{6+}$  concentration for drinking or other domestic purposes, especially in rural areas where water is not treated. Otherwise, the carcinogenic risk of  $\text{Cr}^{6+}$  continues to increase as children grow up.

## Conclusions

Groundwater polluted by nitrogen, fluorine and arsenic has been well known and attracted much attention in the Guanzhong Basin, but high concentrations of  $\text{Cr}^{6+}$  has also been found in recent years. In this study, 13 parameters of 174 groundwater samples were obtained in the Guanzhong Basin. The occurrence and factors influencing the concentration of groundwater  $\text{Cr}^{6+}$  were analyzed. The non-carcinogenic and carcinogenic health risks of groundwater  $\text{Cr}^{6+}$  through drinking water ingestion were assessed. The main conclusions are summarized:

- (1) Groundwater samples from the Guanzhong Basin display  $\text{Cr}^{6+}$  concentrations of 1–220  $\mu\text{g/L}$ . 45.40% and 37.36% of the groundwater samples contain  $\text{Cr}^{6+}$  concentrations ranged  $\leq 10 \mu\text{g/L}$  and 11–50  $\mu\text{g/L}$ , respectively. And they are mainly of  $\text{HCO}_3\text{-Ca}$  and  $\text{HCO}_3\text{-Ca(Mg)}$  type. Around 17.24% present  $\text{Cr}^{6+}$  concentrations exceeding the allowable value for drinking purpose of 50  $\mu\text{g/L}$  and are predominantly classified as  $\text{HCO}_3\text{-Na}$  type. The concentrations of major ions increase with the increase of  $\text{Cr}^{6+}$  concentration interval except  $\text{Ca}^{2+}$ .
- (2) Groundwater with low concentration of  $\text{Cr}^{6+}$  is mainly found in the alluvial aquifer, whereas high concentration of  $\text{Cr}^{6+}$  is associated with the loess aquifer. Low groundwater velocity caused by the low permeability of loess indicates longer residence time of the groundwater, which may favor  $\text{Cr}^{6+}$  generation in loess aquifer.

- (3) Alkaline environment and cation exchange of  $\text{Na}^+$  in sediment against  $\text{Ca}^{2+}$  in the groundwater are more conducive to  $\text{Cr}^{6+}$  formation in groundwater. Industrial activities can discharge a large amount of chromium-containing solid wastes and/or wastewater, and cause the elevation of  $\text{Cr}^{6+}$  concentration in the surrounding groundwater, while fertilizer use in agriculture has no apparent effect on  $\text{Cr}^{6+}$  occurrence in groundwater.
- (4) The non-carcinogenic risk caused by  $\text{Cr}^{6+}$  is low for adults and children through drinking water ingestion. However, the carcinogenic risk is very high, and the carcinogenic risk of  $\text{Cr}^{6+}$  for adults is significantly higher than that for children. Groundwater treatment is necessary to reduce the  $\text{Cr}^{6+}$  concentration for drinking or other domestic purposes, especially in rural areas.

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**Data Availability** All processed data generated or used during the study appear in the submitted article.

## Declarations

**Conflict of interest** The authors declared that they have no conflict of interest.

**Research Involving Human Participants and/or Animals** Not applicable.

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