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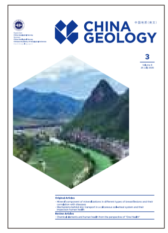

Groundwater metal pollution and health risk assessment in river valley heavy industrial cities of arid regions in China

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A B S T R A C T

Xining, a river valley city in China’s arid region, serves as an important industrial hub with a fragile ecological environment. While groundwater heavy metal pollution in this area has drawn increasing concern, the sources and associated human health risks remain inadequately understood. This study analyzed 144 shallow groundwater samples from urban Xining for 14 heavy metals (Fe, Al, B, Mn, Ba, Zn, Pb, Cr^{6+}, Ni, Cu, Co, Sb, Cd, and As) using the Nemerow comprehensive pollution index, correlation analysis, and the USEPA health risk assessment model. Results identified Fe, Al, B, Mn, Ba, Pb, Cd, and As as the primary pollutants, especially concentrated in river valley plains. These contaminants primarily originate from natural sedimentary conditions and human activities such as industrial and agricultural development. The pollution indices for Al, Pb, Mn, and Fe exceeded clean water thresholds, indicating serious contamination and the need for enhanced regulation. Health risk assessments revealed that children face greater exposure risks than adults, with arsenic and nickel being the main contributors to carcinogenic risk. Sensitivity analysis further showed that As, Fe, and Cd posed the greatest non-carcinogenic and carcinogenic risks, particularly in human-impacted areas such as the Nanchuan and Beichuan valleys and Ganhegou. These findings provide essential insights for groundwater safety management in plateau river valley cities and similar vulnerable regions.

1. Introduction

Groundwater is one of the most important water resources, often regarded as the world’s safest “natural reservoir”, and serves as a vital source of freshwater for human activities (Ali S et al., 2023; An YK and Lu YX, 2018; Benz SA et al., 2024; Fu RJ et al., 2023). With the acceleration of industrialization and the intensified exploitation of mineral resources, heavy metal pollutants have increasingly entered groundwater systems through various pathways such as tailings leachate, industrial wastewater discharge, and agricultural non-point source pollution (Shi HH et al., 2021; Shen HY et al., 2021; You DM et al., 2011). Unlike surface water contamination, groundwater heavy metal pollution is characterized by its hidden nature, slow migration, and long-term accumulation (Zhao D et al., 2023; Lin XF et al., 2021). Once introduced into aquifers, these pollutants pose potential threats to human health through drinking water consumption, bioaccumulation in the food chain, and ecological toxicity (Yao BD et al., 2020; Wallace DR et al., 2020; Cogliano VJ et al., 2011). For instance, cadmium (Cd) can cause kidney damage, osteoporosis, and bone cancer, long-term exposure to hexavalent chromium (Cr^{6+}) may lead to lung cancer, renal dysfunction, and skin lesions, lead (Pb) is associated with neurological disorders, anemia, and kidney disease, and arsenic (As) exposure has been linked to central nervous system disorders, skin cancer, lung cancer, and bladder cancer. Therefore, investigating the characteristics of heavy

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metal pollution in groundwater and conducting health risk assessments are of significant importance.

Health risk assessment methods were first proposed by the United States Environmental Protection Agency (USEPA) in 1976 to evaluate the risks posed by carcinogenic toxic chemicals (Xu Y et al., 2021). Currently, deterministic methods are widely used in health risk assessment, employing standard exposure parameters recommended by the USEPA in combination with contaminant concentration data (Xu KW et al., 2017; Ma J et al., 2023). However, these deterministic approaches struggle to capture the interactive effects of environmental heterogeneity and uncertainty in exposure parameters. As a result, the assessment outcomes may deviate from actual conditions, and the use of fixed parameters often fails to reflect regional variability (Xu KW et al., 2017). In contrast, probabilistic risk assessment (PRA) methods—such as Monte Carlo simulation (MCS) —construct probability distributions for model parameters and generate a full distribution of risk outcomes rather than a single point estimate. This allows for a more comprehensive representation of the probability that a population is at risk and enables quantitative evaluation of uncertainties (Ali S et al., 2023).

Previous studies have demonstrated that health risk assessment of heavy metals in groundwater and soil has become a critical area in environmental science. For example, Di BS et al. (2024) applied Monte Carlo simulation to assess groundwater heavy metal risks in a chemical industrial park in northern Zhejiang, identifying key risk factors and their levels. Wu YN et al. (2024) conducted a health risk evaluation of eight heavy metals in groundwater samples collected from Jiaxing, a water-scarce city in China. Similarly, Zheng LL et al. (2025) adopted this approach to assess health risks from soil heavy metals in eastern Leizhou, Guangdong Province, further validating the applicability of the model. These studies provide valuable methodological references for the present study’s health risk assessment framework.

Xining City is located in the Huangshui River valley on the eastern Tibetan Plateau and represents a typical river valley industrial city in an arid region. With a long history of industrial development dominated by heavy industries —including nonferrous metal smelting, chemical manufacturing, and machinery production —these sectors have significantly contributed to the local economy but also pose considerable risks to the groundwater environment. Groundwater is the primary water supply source for Xining. Rapid urbanization and industrialization have increased water demand, and irrational exploitation has further aggravated groundwater environmental degradation (Li HH, 2022). Xining faces both natural heavy metal anomalies in its groundwater and pollution caused by high vulnerability and intensive contaminant sources (Liu JT et al., 2016). Previous studies have shown pronounced spatial variability in concentrations of heavy metals such as hexavalent chromium, arsenic, iron, and manganese in the shallow groundwater of the region, with pollutant levels in some areas approaching or exceeding safety thresholds (Liu CY et al., 2024a). However, these studies predominantly focus on the distribution and sources of individual heavy metals, with limited attention to the comprehensive pollution status of multiple metals and associated health risks. To address this gap, the present study analyzed 144 shallow groundwater samples from Xining, measuring the concentrations of 14 heavy metals (Fe, Al, B, Mn, Ba, Zn, Pb, Cr^{6+}, Ni, Cu, Co, Sb, and Cd). Using the Nemerow comprehensive pollution index, correlation analysis, and the USEPA health risk assessment model, this work systematically explores the sources and health risks of groundwater heavy metal pollution, providing a scientific basis for metal pollution control and public health protection in arid river valley cities and similar regions.

2. Overview of the study area

Xining City is the central city of the Lanzhou-Xining urban agglomeration and a key industrial hub within the Western Development strategy of China. Its industries are mainly concentrated within several industrial parks encompassing a wide range of sectors, including machinery manufacturing, chemical production, food processing, electronics, light industry, building materials, and metallurgy.

Among these, the Dongchuan Industrial Park focuses on the development of solar photovoltaic manufacturing, electronic thin-film materials, electrolytic copper foil for lithium batteries, and light metal alloy materials, aiming to establish a base for the new energy and advanced materials industries. The Ganhe Industrial Park leverages the province’s abundant mineral and salt lake resources as well as existing industrial foundations to concentrate on the production and deep processing of non-ferrous (and ferrous) metals. The Nanchuan Industrial Park relies on the lithium resource advantages of Qinghai and surrounding provinces to develop a new energy and new materials industrial base centered on lithium battery and optoelectronic production. The Beichuan Industrial Park, located in Datong Hui and Tu Autonomous County, has formed an industrial cluster dominated by non-ferrous metal smelting and rolling, chemical raw material and product manufacturing, power production and supply, and ferrous metal smelting and rolling industries. Due to the constraints of the valley topography, the expansion area of these industrial parks is limited.

Groundwater in Xining can be classified into five types. Pore water in unconsolidated sediments is widely distributed in the mountain-front tilted plain and valley plain areas, primarily as shallow groundwater within Quaternary gravel and pebble layers. There is close hydraulic connectivity between valley groundwater and river water. Clastic rock fissure-pore water mainly exists within Jurassic, Cretaceous, Paleogene, and Neogene clastic rock aquifers. Carbonate rock fissure and karst water is mainly distributed on the northern slope of Laji Mountain in the central and western sections. Bedrock fissure water is primarily found in the Cenozoic clastic rocks, Precambrian metamorphic rocks, and various intrusive rocks' weathered and structural fractures in the hilly areas. The permafrost layer, mostly less than 5 m thick, is mainly located in the western and northern parts of Xining and was not involved in this sampling campaign (Liu CY et al., 2023).

Mountain groundwater is primarily recharged by atmospheric precipitation infiltration, as well as lateral recharge from adjacent bedrock fissure water and surface water, flowing downstream along valleys and discharging as springs. In valley areas, shallow groundwater is mainly recharged by river infiltration and lateral inputs from bedrock mountainous and hilly areas. Some sections also receive recharge from atmospheric precipitation infiltration, leakage from channels, and irrigation infiltration, ultimately flowing into the Huangshui River. The overall groundwater flow direction is from northwest to southeast, with major discharge through anthropogenic groundwater extraction and evaporation.

3. Research methodology

3.1. Sample collection and analysis

Between June 2019 and July 2020, a total of 144 shallow groundwater samples were collected from typical plateau river valley areas within Xining City (Fig. 1). Sampling points covered representative functional zones, including agricultural irrigation areas and residential drinking water sources. The groundwater table depth ranged from 3 m to 45 m, and samples were taken approximately 1 m below the dynamic water level (Liu CY et al., 2024a, 2024b). Using a low-flow well purging method, groundwater was continuously pumped for 5 minutes with a submersible pump to remove stagnant water in the wells, ensuring the collection of representative *in-situ* groundwater samples.

Following groundwater quality analysis protocols (DZ/T0064.2-2021), samples were immediately stored in pre-

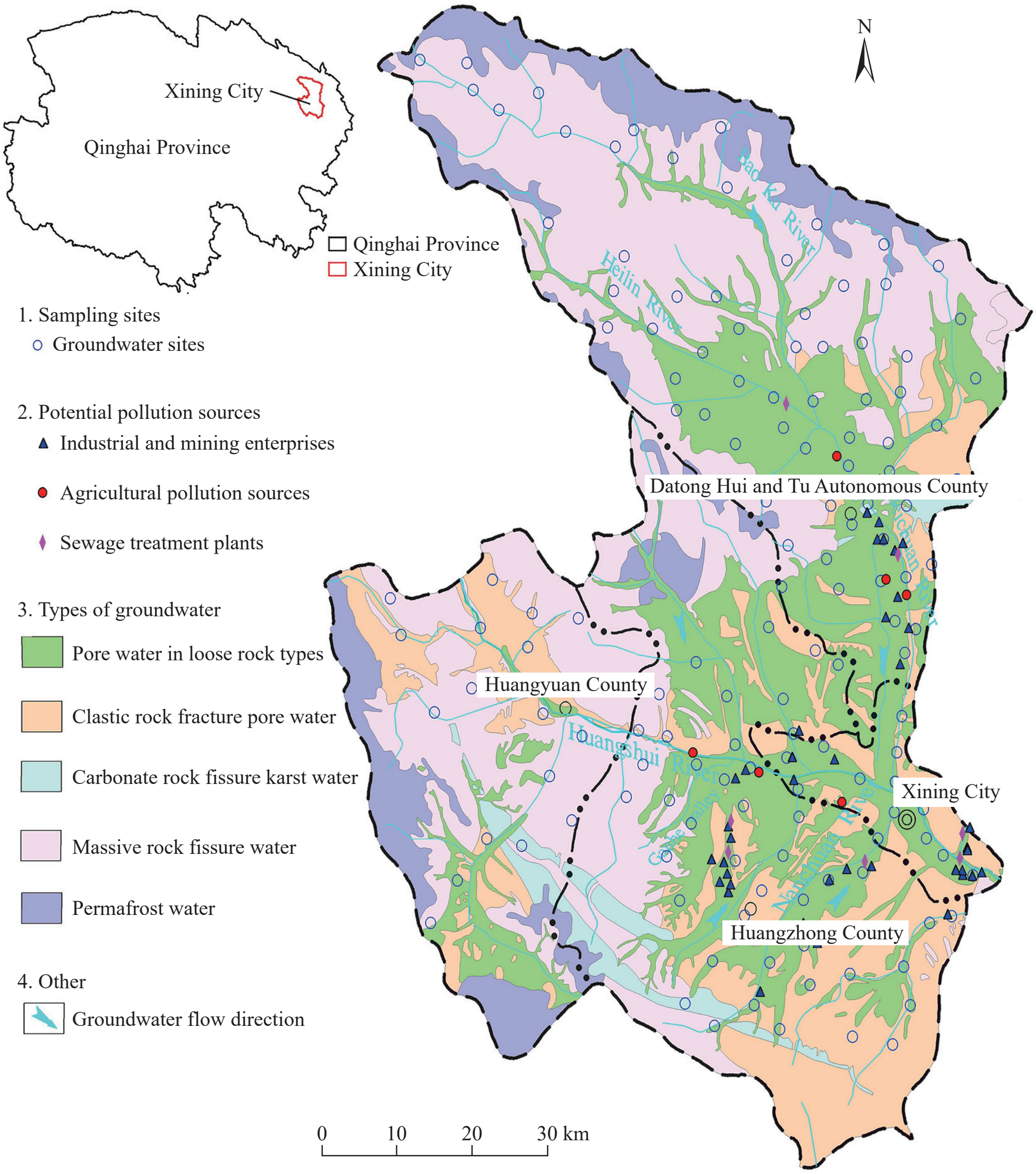

Fig. 1. Sampling points distribution map in Xining City.

cleaned 2.5 L high-density polyethylene bottles. Nitric acid was added to adjust the pH to below 2, and samples were kept at 4°C in the dark before being delivered within 7 days to the Groundwater, Mineral Water, and Environmental Monitoring Center laboratory of the Chinese Academy of Geological Sciences.

Laboratory analysis of 14 heavy metal elements—including Fe, Al, and B—was conducted following the standards outlined in "Methods for Testing Natural Drinking Mineral Water" (GB/T 8538 —2016), using the methods listed in Table 1. Dynamic parameters such as water temperature, pH, redox potential (Eh), and dissolved oxygen (DO) were measured on-site with a portable multiparameter water quality analyzer (WTW Multi 340i/SET, Germany) to minimize alterations in water quality during transportation.

3.2. Evaluation criteria and methods

3.2.1. Pollution evaluation

The single-factor pollution index and the Nemero comprehensive pollution index (Han XM, 2023) were used to evaluate the heavy metal pollution levels in groundwater. The single-factor pollution index is defined as the ratio of the measured concentration of a heavy metal element in groundwater to its corresponding reference standard value. The Nemero comprehensive pollution index reflects the overall pollution level at a sampling site by considering both the maximum and average values of the single-factor pollution indices. The calculation formulas are as follows (Equs 1, 2):

$$p_i = \frac{C_i}{S_i} \tag{1}$$

$$N_i = \sqrt{\frac{(P_{imax})^2 + (P_{iadv})^2}{2}} \tag{2}$$

where: i represents a heavy metal element, pi is the pollution index of element i, Ci is the measured concentration of heavy metal element i, Si is the Class III concentration threshold value in the "Groundwater Quality Standard" (GB/T 14848-2017), Ni is the Nemero comprehensive pollution index.

The classification scheme for the single-factor pollution index and Nemero comprehensive pollution index is shown in Table 2.

3.2.2. Monte carlo health risk assessment

Health risk assessment primarily evaluates the non-carcinogenic and carcinogenic risks of heavy metal elements by calculating exposure doses and their associated sensitivities. The three main exposure pathways for heavy metals entering the human body are hand-to-mouth ingestion, inhalation, and dermal contact. Since heavy metals in groundwater are mainly ingested through drinking water, this study considers only the health risks associated with drinking water exposure. Based on the health risk assessment model recommended by the U.S. EPA (Metropolis N et al., 1949), the carcinogenic and non-carcinogenic health risks for residents of Xining City were evaluated using the following formulas (Equ 3):

$$ADD = \frac{C_w \times IR \times EF \times ED}{BW \times AT} \tag{3}$$

Where ADD represents the average daily intake of heavy metals through drinking water, C_W is the measured concentration of heavy metal element iii in groundwater. Detailed parameters are listed in Table 3. The formulas for calculating the non-carcinogenic risk (*HI*) and carcinogenic risk (*TCR*) of heavy metals in groundwater are as follows (Equs 4, 5):

$$HI = \Sigma HQ = \Sigma\frac{ADD\mathrm{i}}{RfD\mathrm{i}} \tag{4}$$

$$TCR = \Sigma CR = \Sigma ADD\mathrm{i} \times SF\mathrm{i} \tag{5}$$

In the formulas, *HI* and *HQ* represent the cumulative and individual non-carcinogenic risk indices, respectively, *TCR* and *CR* represent the cumulative and individual carcinogenic risk indices, respectively. ADD_i is the daily average exposure dose of heavy metal element iii for both non-carcinogenic and carcinogenic risks. RfD_i is the reference dose for non-carcinogenic risk via oral ingestion (mg/(kg·day)), and SF_i is the carcinogenic slope factor for oral ingestion of element iii. Reference values for RfD and *SF* are listed in Table 4 (Li JF et al., 2023; Ma J et al., 2023).

Table 1. Laboratory element analysis and testing methods.

Element (s)	Laboratory analysis method	Precision/Error margin
Fe, Al, Ni	Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)	⩽±3%
B	Ion Chromatography (IC)	⩽±5%
Mn, Ba, Zn, Ni, Cu, Co, Cd, Pb, Cr^{6+}, Sb, As	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	⩽±5%

Table 2. Pollution index grade of single and comprehensive Nemerow.

P_i	Pollution level (Single-Factor)	N_i	Pollution level (Nemero)	Overall pollution level
P_i⩽0.7	No pollution	N_i⩽0.7	No pollution	Clean
0.7<P_i⩽1.0	Alert level	0.7<N_i⩽1.0	Alert level	Near clean
1.0<P_i⩽2.0	Light pollution	1.0<N_i⩽2.0	Light pollution	Light pollution
2.0<P_i⩽3.0	Moderate pollution	2.0<N_i⩽3.0	Moderate pollution	Moderate pollution
P_i>3.0	Severe pollution	N_i>3.0	Severe pollution	Severe pollution

Table 3. Calculation parameters of human in take of heavy metals.

Parameter	Meaning	Unit	Probability Distribution	Reference value		
				Children (0–17 years)	Adults (≥18 years)	Data Source
C_W	Average concentration of metal element	mg/L	Lognormal	–	–	Measured values
IR	Average daily drinking water intake	L/d	Triangular	1	1.542	Duan XL et al., 2014
EF	Exposure frequency	d/a	Lognormal	350	350	Duan XL et al., 2014, 2016
ED	Exposure duration	a	Custom distribution	9	30	Duan XL et al., 2014, 2016
AT	Averaging time	d	Custom distribution	25500	25500	Duan XL et al., 2014, 2016
ET	Exposure time	h/d	Custom distribution	0.4167	0.6333	Duan XL et al., 2014, 2016
BW	Body weight	kg	Lognormal	24	57	Duan XL et al., 2014, 2016

Table 4. Values of parameters related to health risk assessment.

Element	Non-carcinogenic reference dose RfD (mg/(kg·d))	Carcinogenic slope factor SF (mg/(kg·d))	Exposure duration ED (years)	Averaging time AT (days)	References
As	3.00E-04	1.51	70	25550	Abbott BW et al., 2016; Wang SL et al., 2024
Cd	5.00E-04	6.10	–	–	Abbott BW et al., 2016; Wang XD et al., 2022; Wang SL et al., 2024
Cr^{6+}	3.00E-03	0.50	–	–	Di BS et al., 2024
B	2.00E-01	–	–	–	Ahmad W, 2021
Al	1.40E-01	10.00	–	–	Ahmad W, 2021; Wang SL et al., 2024
Cu	4.00E-02	1.70	–	–	Abbott BW et al., 2016; Wang SL et al., 2024
Hg	3.00E-04	1.80	–	–	Kan XQ et al., 2021; Wang SL et al., 2024
Pb	1.40E-03	8.50E-03	–	–	Wang XD et al., 2022; Wang SL et al., 2024
Zn	3.00E-01	0.60	–	–	Abbott BW et al., 2016
Mn	4.60E-03	–	–	–	Di BS et al., 2024
Fe	3.00E-01	0.10	–	–	Yan ZY et al., 2023; Wang SL et al., 2024
Ni	2.00E-02	1.70	–	–	Di BS et al., 2024; Kan et al., 2021
Ba	2.00E-01	–	–	–	Ahmad W, 2021
Co	3.00E-04	–	–	–	Di BS et al., 2024
Sb	4.00E-04	–	–	–	Ahmad W, 2021

When $HI \leqslant 1$, the non-carcinogenic risk is considered negligible, otherwise, a potential non-carcinogenic risk exists. When $TCR \leqslant$1.00E-6, the carcinogenic risk is negligible, when 1.00E-6<$TCR \leqslant$1.00E-4, a tolerable carcinogenic risk is present, and when TCR>1.00E-4, an intolerable carcinogenic risk exists.

3.3. Data processing

Data processing and statistical analysis were performed using SPSS 26 software. Monte Carlo simulations with 10000 iterations were conducted in Excel 2016 using the Oracle Crystal Ball 11 add-in to obtain *ADD*, *HI*, and *CR* values. Graphs and Figures were produced using CorelDRAW 2021 and Origin 2021 software.

4. Result and discussion

4.1. Statistics of heavy metal concentrations in groundwater

The statistical results of heavy metal concentrations in groundwater around Xining City are shown in Table 5. Except for mercury (Hg), which was not detected and thus excluded from further analysis and evaluation, the average concentrations of the remaining 14 detected elements were ranked in descending order as follows: Fe > Al > B > Mn > Ba > Zn > As > Pb > Cr^{6+} > Ni > Cu > Co > Sb > Cd (see Table 5).

According to the Class III limits of the “Groundwater Quality Standard” (GB/T14848-2017), the detection rates in descending order were Al, Fe, B, Ba, Mn, Sb, Zn, As, Pb, Ni, Cr^{6+}, Cd, Cu, and Co. Among these, seven heavy metals—Cd, $Cr^{6+,}$ Cu, Hg, Zn, Co, and Sb—did not exceed the Class III groundwater quality standard limits. However, the exceedance rates for Al, Fe, Ba, Mn, Pb, B, As, and Ni were 22.22%, 20.83%, 16.67%, 9.72%, 8.33%, 7.63%, 1.39%, and 1.39%, respectively.

The single-factor pollution index values ranked from highest to lowest are: Fe (P_i = 6.79), Pb (P_i = 2.17), Mn (P_i = 2.09), Al (P_i = 1.96), Ba (P_i = 0.86), B (P_i = 0.69), As (P_i = 0.46), Cd (P_i = 0.46), Cu (P_i = 0.44), Ni (P_i = 0.42), Sb (P_i = 0.39), Zn (P_i = 0.37), Co (P_i = 0.34), and Cr^{6+} (Pi = 0.23) (see Table 6).

Among these, the single-factor pollution index of Fe exceeds 3, indicating heavy pollution. Pb and Mn have indices between 2 and 3, indicating moderate pollution. Al’s index falls between 1 and 2, indicating light pollution. Ba’s pollution index corresponds to a warning level, with the pollution status classified as "almost clean."

The other nine heavy metals—B, As, Cd, Cu, Ni, Sb, Zn, Co, and Cr^{6+}—all have single-factor pollution indices below 0.7, which, according to the classification standards, indicates no pollution (see Fig. 2).

Table 5. Concentration of heavy metals in the groundwater in the study area.

Heavy metal element	Min value /(mg/L)	Max value /(mg/L)	Mean value /(mg/L)	Median /(mg/L)	Coefficient of variation (CV)	Detection vate /%	Class III standard limit /(mg/L)	Exceedance rate /%	Detection limit /(mg/L)
As	ND.	8.6E-2	1.9E-3	0	1.0E-2	2.1E+1	5.0E-2	1.4	5.0E-4
Cd	ND.	1.2E-3	2.7E-5	0	1.4E-4	5.6	5.0E-3	0.0	1.0E-4
Cr^{6+}	ND.	2.9E-2	1.4E-3	0	4.2E-3	1.2E+1	5.0E-2	0.0	1.0E-3
B	9.8E-3	5.5	3.0E-1	1.6E-2	5.6E-1	5.6E+1	5.0E-1	7.6	5.0E-3
Al	ND.	1.7E+1	4.2E-1	7.2E-2	1.7E+0	9.9E+1	2.0E-1	2.2E+1	1.0E-2
Cu	ND.	2.6E-2	8.0E-4	0	4.0E-3	4.9	1.0	0.0	5.0E-4
Hg	ND.	ND.	-	-	-	-	1.0E-3	0.0	1.0E-5
Pb	ND.	1.8E-1	3.8E-3	0	1.7E-2	1.8E+1	1.0E-2	8.3	5.0E-4
Zn	ND.	3.2E-1	1.1E-2	0	4.4E-2	2.2E+1	1.0	0.0	1.0E-3
Mn	ND.	4.2	8.0E-2	0	3.9E-1	4.4E+1	1.0E-1	9.7	5.0E-4
Fe	ND.	1.0E+2	1.5	5.1E-2	9.3E+0	7.5E+1	3.0E-1	2.1E+1	1.0E-2
Ba	ND.	3.7E-1	7.9E-2	1.8E-2	6.4E-2	5.6E+1	1.0E-1	1.7E+1	1.0E-3
Co	ND.	2.1E-2	4.6E-4	0	2.1E-3	2.1	5.0E-2	0.0	5.0E-4
Sb	ND.	2.1E-3	2.5E-4	0	2.6E-4	4.1E+1	5.0E-3	0.0	1.0E-5
Ni	ND.	2.7E-2	1.2E-3	0	3.3E-3	1.3E+1	2.0E-2	1.4	5.0E-4

Notes: “ND.” stands for “Not Detected”, “-” stands for “Not Applicable” or “None”.

Table 6. Evaluation of the heavy metals risk index.

Element	Fe	Al	Pb	Mn	B	Ba	As	Sb	Zn	Cu	Cr^{6+}	Cd	Ni	Co
Single-factor Pollution Index (Pi)	6.79	1.96	2.17	2.10	0.69	0.86	0.46	0.39	0.37	0.44	0.23	0.46	0.42	0.34
Nemerow Integrated Pollution Index (Ni)	22.0	3.9	2.8	1.9	1.4	1.3	1.1	0.80	0.69	0.00	0.00	0.00	0.00	0.00
Pollution Degree	Heavy pollution	Heavy pollution	Moderate pollution	Light pollution	Light pollution	Light pollution	Light pollution	Alert level	Alert level	No pollution	No pollution	No pollution	No pollution	No pollution
Pollution Level	Severely polluted	Severely polluted	Moderately polluted	Beginning pollution	Beginning pollution	Beginning pollution	Beginning pollution	Almost clean	Almost clean	Clean	Clean	Clean	Clean	Clean

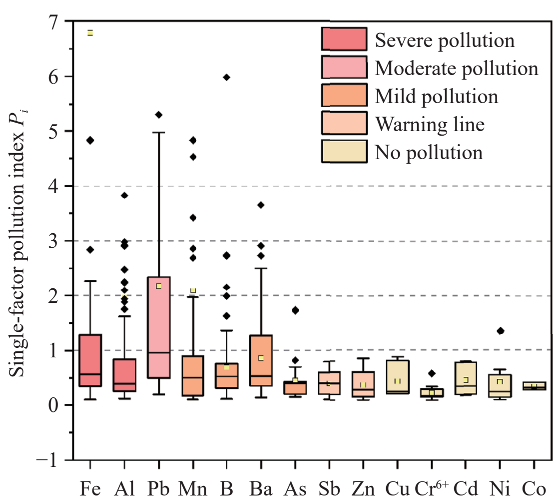

Fig. 2. Box plots of single-factor contamination indices (P_i) of heavy metals in groundwater in the study area.

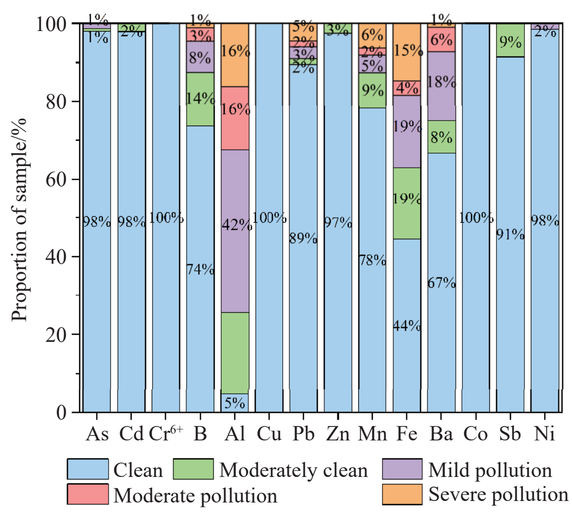

Fig. 3. Based on the Heavy Metal Nemero Comprehensive Pollution Index (N_i), the statistical chart of the proportion of points with different levels of pollution index.

Based on the Nemerow index method, the proportion of groundwater sampling points at different pollution levels is shown in Fig. 3. For the three heavy metals Cr^{6+}, Cu, and Co, all sampling points fall within the $N_i \leqslant 0.7$ range, indicating a “clean” status. Among As, Cd, Zn, Sb, and Ni, the majority of sampling points also show pollution indices within the $N_i \leqslant 0.7$ (clean) category. In contrast, the proportions of sampling points with $N_i \leqslant 0.7$ for Al, Fe, Mn, Ba, B, and Pb are relatively low, at 5%, 44%, 67%, 74%, and 89%, respectively. Moreover, the proportions of sampling points where the single-factor pollution index *Pi* reaches or exceeds 3.0 for Al, Fe, Mn, and Pb are 16%, 15%, 6%, and 5%, respectively. This indicates that these heavy metals exhibit relatively severe pollution levels in the groundwater.

4.2. Spatial distribution characteristics of heavy metals in groundwater

Multiple heavy metal indicators may influence the groundwater sampling sites' pollution status in the study area. This study presents only the most prominent pollution indicators spatially (Fig. 4). Combining Fig. 3 and Fig. 4, it is clear that groundwater pollution in the study area is mainly affected by heavy metals Al, Fe, Ba, B, Mn, Pb, and As, predominantly distributed in the river valley plain areas.

The heavy metals with a comprehensive pollution index $N_i > 10$ are Fe and Al. Fe is mainly distributed in the central Huangshui River valley area of Huangzhong County, suburban areas around Datong County city, and Xining city. This is primarily due to the original sedimentary environment, with some local influence from human activities. Previous research has confirmed that groundwater iron exceedance in Xining's construction land is high (Liu CY et al., 2024a).

Al is mainly distributed along river valleys and is influenced by various natural and anthropogenic factors. Geological surveys show that the surrounding geology of Xining consists mainly of sedimentary rocks, granite, and metamorphic rocks. Al-bearing minerals such as feldspar, mica, and clay minerals release aluminum ions (Al^{3+}) during weathering, which enter the aquifers via groundwater flow. Additionally, Xining's industries including electrolytic Al, metallurgy, and chemical sectors may discharge Al-containing wastewater, which can pollute groundwater through infiltration or surface runoff.

Ba is primarily distributed in the northeast of Datong County. Some strata in the Qilian Mountain fold belt (e.g., Cambrian and Ordovician carbonate rocks) may be rich in barium. Groundwater dissolves and transports Ba into the valley areas. Industrial discharges, mining waste, and

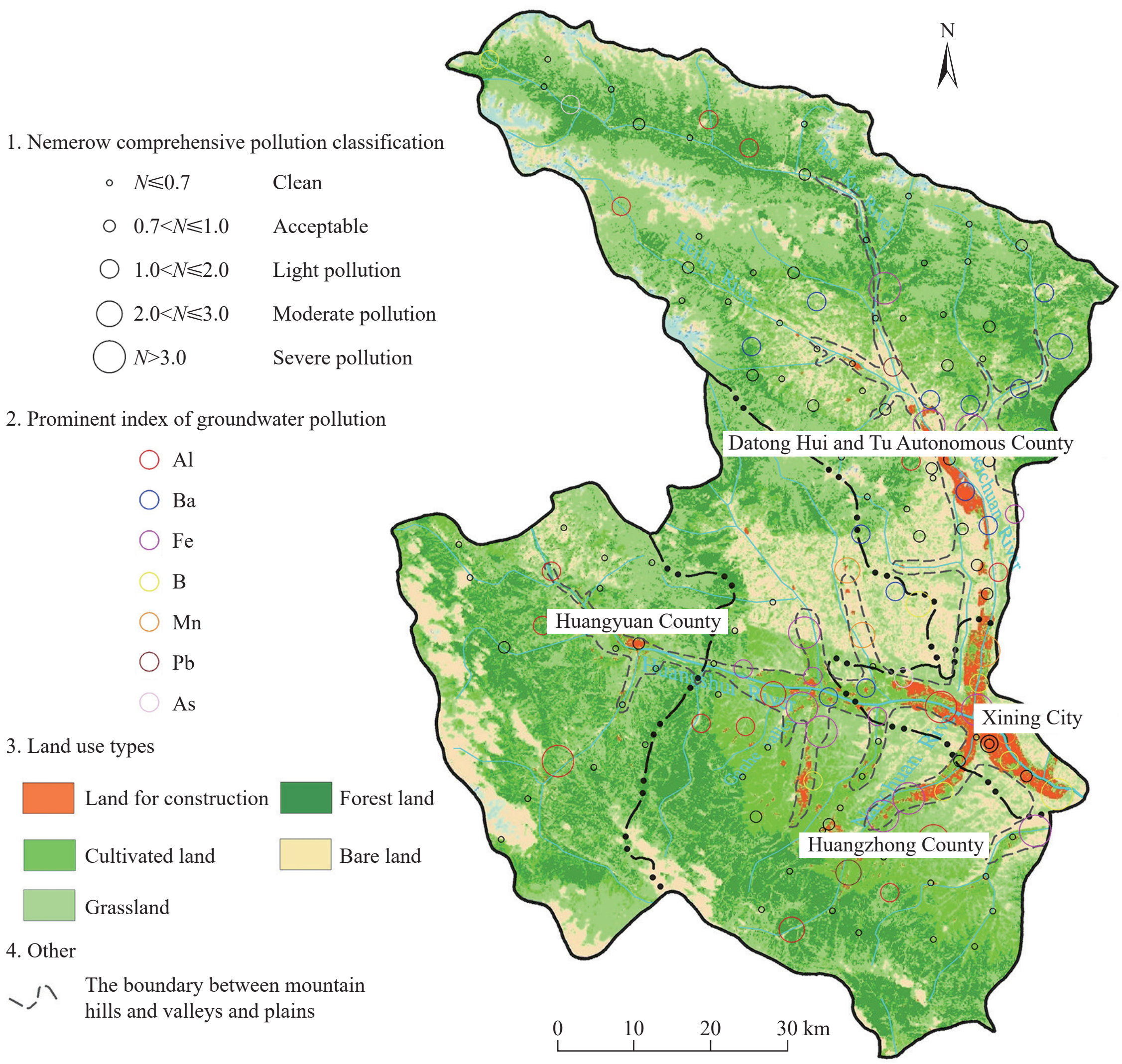

Fig. 4. Spatial distribution characteristics of prominent indicators of groundwater pollution.

agricultural activities may also contribute Ba pollution. Industrial activities in Datong County, such as chemical, electronics manufacturing, and metal processing industries, particularly those producing or using barium salts, may discharge barium-containing wastewater, which accumulates in the river valleys through runoff.

B is mainly distributed in the northwest of Xining and Datong County, where boron-rich rocks (such as evaporites and shales) and Quaternary loose sediments are present. B enters the groundwater system through rock weathering and mineral dissolution (e.g., borax, tourmaline). Local industries such as chemical and metallurgical sectors in Xining may release boron-containing wastewater (e.g., from glass manufacturing and detergent production), potentially contaminating groundwater through leakage or direct discharge.

Mn's distribution is similar to Fe, mainly concentrated in the valley areas used for construction land, affected by both natural and human factors.

Pollution hotspots for Pb and As are fewer (Pb has two locations, but 10 points where it co-occurs with Fe, Al, etc., As has only one location), mainly distributed in the Nanchuan River valley, Beichuan River valley of Huangzhong County, and the Gan River valley south of Huangshui River. These may be influenced by human activities (Liu HZ et al., 2015).

4.3. Analysis of heavy metal sources

The results of Pearson correlation analysis among heavy metal elements are shown in Fig. 5. At the significance level of P ⩽ 0.01, the correlation coefficients between Fe and Mn, Cu, Zn, Cd, Ni, and Co are 0.97, 0.82, 0.63, 0.85, 0.73, and 0.84, respectively. This indicates significant positive correlations between Fe and these six elements, suggesting that these seven elements may share a common source or similar migration processes. The correlation coefficient between Pb and Al is 0.85, indicating that these two elements may also have the same source or similar migration pathways.

Using principal component analysis (PCA), the sources of heavy metals in groundwater can be further elucidated. The KMO value (0.806) and Bartlett's test of sphericity ($p < 0.001$) indicate that the dataset of 14 heavy metal elements is suitable for PCA. As shown in Table 7 and Table 8, four principal components were identified from the PCA of groundwater heavy metals, explaining a total variance of 76.14%.

The contribution rate of Principal Component 1 is 48.111%. Fe, Mn, Cu, Zn, Cd, Ni, and Co have high loadings with weight coefficients of 0.936, 0.917, 0.710, 0.781, 0.900, 0.665, and 0.795 respectively, indicating strong correlations among these seven metal elements, consistent with the Pearson correlation analysis results. The main industries in Xining City are metal processing and electroplating. During metal processing and electroplating production, Cu, Zn, Cd, Ni, and Co commonly appear in electroplating wastewater, metal pickling effluents, or alloy manufacturing processes, especially Cd, Ni, and Co. Additionally, the geological background of sedimentary rocks may lead to natural

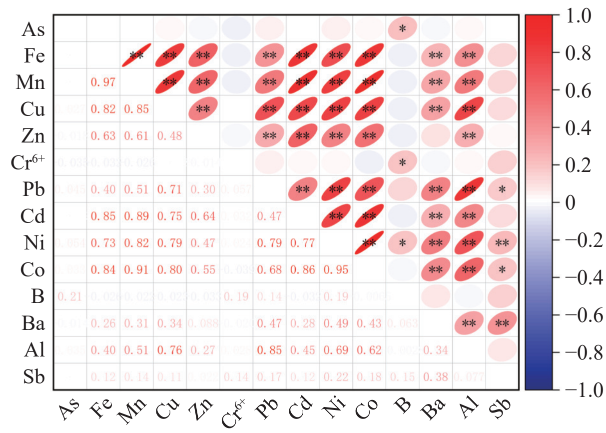

Fig. 5. Pearson correlation of quality parameters in groundwater. Note: *stands for P≤0.05, **stands for P≤0.01.

Table 7. Principal component analysis of heavy metals in groundwater.

Component	Component			Initial eigenvalue			Extracted sum of squared loadings		
	Eigenvalue	Variance /%	Cumulative Variance /%	Eigenvalue	Variance /%	Cumulative Variance /%	Eigenvalue	Variance /%	Cumulative Variance /%
1	6.735	48.111	48.111	6.735	48.111	48.111	4.898	34.987	34.987
2	1.622	11.584	59.694	1.622	11.584	59.694	3.202	22.872	57.859
3	1.187	8.478	68.172	1.187	8.478	68.172	1.344	9.601	67.461
4	1.116	7.97	76.141	1.116	7.97	76.141	1.215	8.681	76.141
5	0.999	7.137	83.279	—	—	—	—	—	—
6	0.715	5.104	88.383	—	—	—	—	—	—
7	0.526	3.76	92.143	—	—	—	—	—	—
8	0.503	3.595	95.738	—	—	—	—	—	—
9	0.279	1.992	97.73	—	—	—	—	—	—
10	0.143	1.019	98.749	—	—	—	—	—	—
11	0.102	0.73	99.479	—	—	—	—	—	—
12	0.046	0.328	99.808	—	—	—	—	—	—
13	0.014	0.1	99.907	—	—	—	—	—	—
14	0.013	0.093	100	—	—	—	—	—	—

Note: "—" indicates that components with eigenvalues less than 1 were not extracted or rotated.

enrichment of Fe, Mn, Co, and Ni. In mining and metallurgy industries, tailings leachate and ore beneficiation wastewater may release Fe and Mn (naturally redox-sensitive elements), as well as Cu, Zn, Cd, Ni, and Co (elements associated with ores). Under reducing conditions, the reductive dissolution of Fe (Mn) oxides may release adsorbed Cu, Zn, Cd, Ni, and Co. Therefore, Principal Component 1 is inferred to reflect the combined influence of natural factors and industrial activities.

The contribution rate of Principal Component 2 is 11.584%. Pb, Ba, and Al have high loadings with weight coefficients of 0.876, 0.639, and 0.841 respectively. These elements are mainly distributed in the river valley plain area of Datong County, where human activities are frequent. According to investigations, Datong County is a base for the electrolytic Al industry. Industries such as electrolytic Al, metallurgy, and chemical manufacturing may discharge Al-containing wastewater, which can contaminate groundwater through leakage or surface runoff. Pb may originate from lead-acid battery manufacturing. Ba (barium) may be related to glass manufacturing or industrial waste residue leachate, especially from companies producing or using barium salts, potentially discharging barium-containing wastewater that accumulates in the river valley area via runoff. In summary, Principal Component 2 is inferred to represent the impact of industrial wastewater.

Table 8. Factor loadings of heavy metal elements in groundwater.

Heavy Metal Element	Principal Component 1	Principal Component 2	Principal Component 3	Principal Component 4
As	0.001	0.04	–0.126	0.788
Fe	0.936	0.197	0.039	–0.035
Mn	0.917	0.317	0.035	–0.022
Cu	0.71	0.583	–0.055	0.019
Zn	0.781	-0.025	–0.021	–0.008
Cr^{6+}	0.031	-0.114	0.582	0.172
Pb	0.293	0.876	0.035	0.127
Cd	0.9	0.249	0.061	–0.018
Ni	0.665	0.657	0.142	0.122
Co	0.795	0.532	0.055	–0.006
B	-0.046	0.048	0.429	0.691
Ba	0.079	0.639	0.398	–0.187
Al	0.295	0.841	–0.133	0.073
Sb	0.032	0.215	0.771	–0.123

The contribution rate of Principal Component 3 is 8.478%. Cr^{6+} and Sb have high loadings with weight coefficients of 0.582 and 0.771, respectively. Both heavy metals are highly toxic. Cr^{6+} may originate from wastewater discharge from electroplating plants, while Sb may come from alloy manufacturing. The combination of Cr^{6+} and Sb likely points to specific industrial point-source pollution, and attention should be paid to the localized enrichment of these highly toxic elements. Therefore, Principal Component 3 is inferred to represent specific industrial activities.

The contribution rate of Principal Component 4 is 7.970%. As and B have high loadings with weight coefficients of 0.788 and 0.691, respectively. Arsenic (As) may originate from arsenic-containing pesticides and fertilizers, while boron (B) is commonly found in boron-containing fertilizers or irrigation wastewater. Therefore, Principal Component 4 is inferred to represent agricultural pollution sources.

4.4. Based on Monte Carlo simulation: Health risk assessment of heavy metals in groundwater

Monte Carlo simulation was conducted using Oracle Crystal Ball 11 software, with the number of trials set to 10000 and a confidence level of 95%. Non-carcinogenic risk, carcinogenic risk, and sensitivity analyses were performed for the health risks posed by heavy metals in groundwater.

4.4.1. Non-carcinogenic health risk assessment of heavy metals in groundwater

Non-carcinogenic health risk assessment of heavy metals detected in groundwater is presented in Table 9. The 95th

Table 9. Assessment of non-carcinogenic health risks of heavy metals in groundwater.

Heavy metal element	HQP_5		HQP_{95}		HQ_{mean}		Contribution rate /%
	Adult	Child	Adult	Child	Child	Adult	
Al	5.86E-2	9.01E-2	1.11E-1	1.71E-1	1.26E-1	8.20E-2	12.61
As	1.23E-1	1.90E-1	2.35E-1	3.62E-1	2.66E-1	1.73E-1	26.62
B	2.91E-2	4.50E-2	5.56E-2	8.54E-2	6.31E-2	4.10E-2	6.31
Ba	2.20E-2	3.41E-2	4.21E-2	6.46E-2	4.75E-2	3.09E-2	4.75
Cd	5.27E-4	8.11E-4	9.99E-4	1.55E-3	1.14E-3	7.37E-4	0.11
Co	2.30E-2	2.30E-2	4.36E-2	4.36E-2	3.21E-2	3.21E-2	3.89
Cr	9.09E-3	1.40E-2	1.72E-2	2.66E-2	1.96E-2	1.27E-2	1.96
Cu	3.89E-4	5.99E-4	7.39E-4	1.14E-3	8.39E-4	5.45E-4	0.08
Fe	1.01E-1	1.57E-1	1.82E-1	2.80E-1	2.12E-1	1.37E-1	21.16
Mn	3.41E-2	5.22E-2	6.48E-2	9.89E-2	7.27E-2	4.74E-2	7.28
Ni	5.85E-4	9.04E-4	1.11E-3	1.73E-3	1.27E-3	8.21E-4	0.13
Pb	5.28E-2	8.12E-2	1.00E-1	1.54E-1	1.14E-1	7.40E-2	11.40
Sb	1.21E-2	1.88E-2	2.31E-2	3.59E-2	2.63E-2	1.71E-2	2.63
Zn	7.14E-4	1.10E-3	1.37E-3	2.09E-3	1.54E-3	1.00E-3	0.15
Total *HI*	8.67E-1	5.76E-1	1.12	7.39E-1	9.92E-1	6.57E-1	100.00

percentile (P95) of the non-carcinogenic health risk index (*HQ*) for heavy metals in groundwater in Xining City are all less than 1. The average *HQ* values for adults are ranked as follows: As > Fe > Al > Pb > Mn > B > Co > Ba > Sb > Cr > Zn > Ni > Cd > Cu. For children, the ranking is: As > Fe > Al > Pb > Mn > B > Ba > Co > Sb > Cr > Zn > Ni > Cd > Cu, indicating that arsenic (As) is the primary heavy metal causing non-carcinogenic health risks among different population groups in the study area.

From Table 9, the mean non-carcinogenic health risk index for children (*HI* = 9.92E-1) is higher than that for adults (*HI* = 6.57E-1). According to the probability distribution of non-carcinogenic risk in groundwater shown in Fig. 6, the 95th percentile of the adult *HI* (7.39E-1) is less than 1, which does not exceed the non-carcinogenic risk threshold of 1. This indicates that the non-carcinogenic health risk of heavy metals in groundwater for adults in Xining City is negligible. However, the 95th percentile *HI* value for children (1.12) exceeds the threshold of 1, suggesting that heavy metals in groundwater pose a non-carcinogenic health risk to children in Xining City.

Based on the weighted calculation of the mean non-carcinogenic health risk of various heavy metals in groundwater, arsenic (As), iron (Fe), and aluminum (Al) contribute the most to the non-carcinogenic health risk (Table 9). Among them, arsenic has the highest contribution at 26.62%, indicating its dominant role in the non-carcinogenic health risk from groundwater in Xining City and the need for targeted attention and control. The contributions of iron and aluminum are 21.16% and 12.61%, respectively, also accounting for a significant proportion and having a notable impact on health risk.

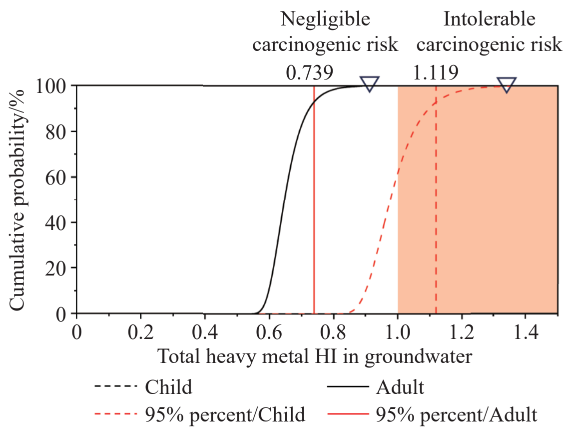

Fig. 6. Probability distribution for non-carcinogenic risk (*HI*) of heavy metals in groundwater.

4.4.2. Carcinogenic health risk assessment of heavy metals in groundwater

The carcinogenic health risk assessment results of heavy metals in groundwater in Xining City (Table 10; Fig. 7) show that the average carcinogenic risk index (*CR*) of the five heavy metals follows the order: As > Ni > Cd > Cr > Pb, with children exhibiting higher carcinogenic risks than adults. Arsenic (As) and nickel (Ni) account for 56.17% and 39.73% of the total carcinogenic health risk index, respectively (Table 10). In western and northern China, As is widely recognized as the heavy (or metalloid) metal with the highest carcinogenic risk. Besides these metals, mercury (Hg) pollution has also been reported in other regions such as Gansu (Wang L et al., 2024).

For both adults and children, the mean values and 95th percentile values of As and Ni exceed 1.00E-6, with maximum values greater than 1.00E-4, indicating that these two elements pose an unacceptable carcinogenic risk to both populations. For cadmium (Cd) and lead (Pb), the mean values and 95th percentile values are above 1.00E-6 but the maximum values are below 1.00E-4, suggesting these two elements pose an acceptable carcinogenic risk to adults and children. Chromium (Cr) shows mean and 95th percentile values below 1.00E-6 for both adults and children, indicating that Cr's carcinogenic risk can be considered negligible for the Xining population.

The total carcinogenic risk index (*TCR*) indicates that the average *TCR* values for adults and children are 1.39E-4 and 2.15E-4, respectively. The 95th percentile values of the carcinogenic risk index for adults and children are 1.74E-4 and 2.72E-4, respectively, all exceeding the threshold value of 1.00E-4. This indicates that groundwater heavy metals in Xining pose a certain unacceptable carcinogenic risk to both adults and children. Additionally, children's *TCR* is approximately 1.5 to 2.0 times that of adults, and for both groups, the 95th percentile *TCR* is about 1.6 times the 5th percentile, suggesting some variability in carcinogenic risk among individuals.

4.4.3. Sensitivity analysis

Sensitivity analysis compares the influence of various parameters on health risks and quantifies the main contributing factors. The magnitude of the values is closely related to the risk outcomes, the larger the value, the higher the risk. A positive value indicates a positive correlation with

Table 10. Health risk assessment of carcinogens from heavy metals in groundwater.

Heavy metal element	CRP_5		CRP_{95}		CR_{mean}		Contribution Rate /%
	Adult	Child	Adult	Child	Adult	Child	
As	5.45E-5	8.26E-5	1.07E-4	1.70E-4	7.75E-5	1.21E-4	56.17
Ni	3.88E-5	6.03E-5	7.59E-5	1.17E-4	5.52E-5	8.52E-5	39.73
Cd	3.14E-6	4.85E-6	6.10E-6	9.47E-6	4.45E-6	6.89E-6	3.21
Cr	2.66E-7	4.09E-7	4.90E-7	7.57E-7	3.65E-7	5.63E-7	0.26
Pb	6.34E-7	9.80E-7	1.17E-6	1.82E-6	8.72E-7	1.35E-6	0.63
TCR	1.09E-4	1.68E-4	1.74E-4	2.72E-4	1.39E-4	2.15E-4	100.0%

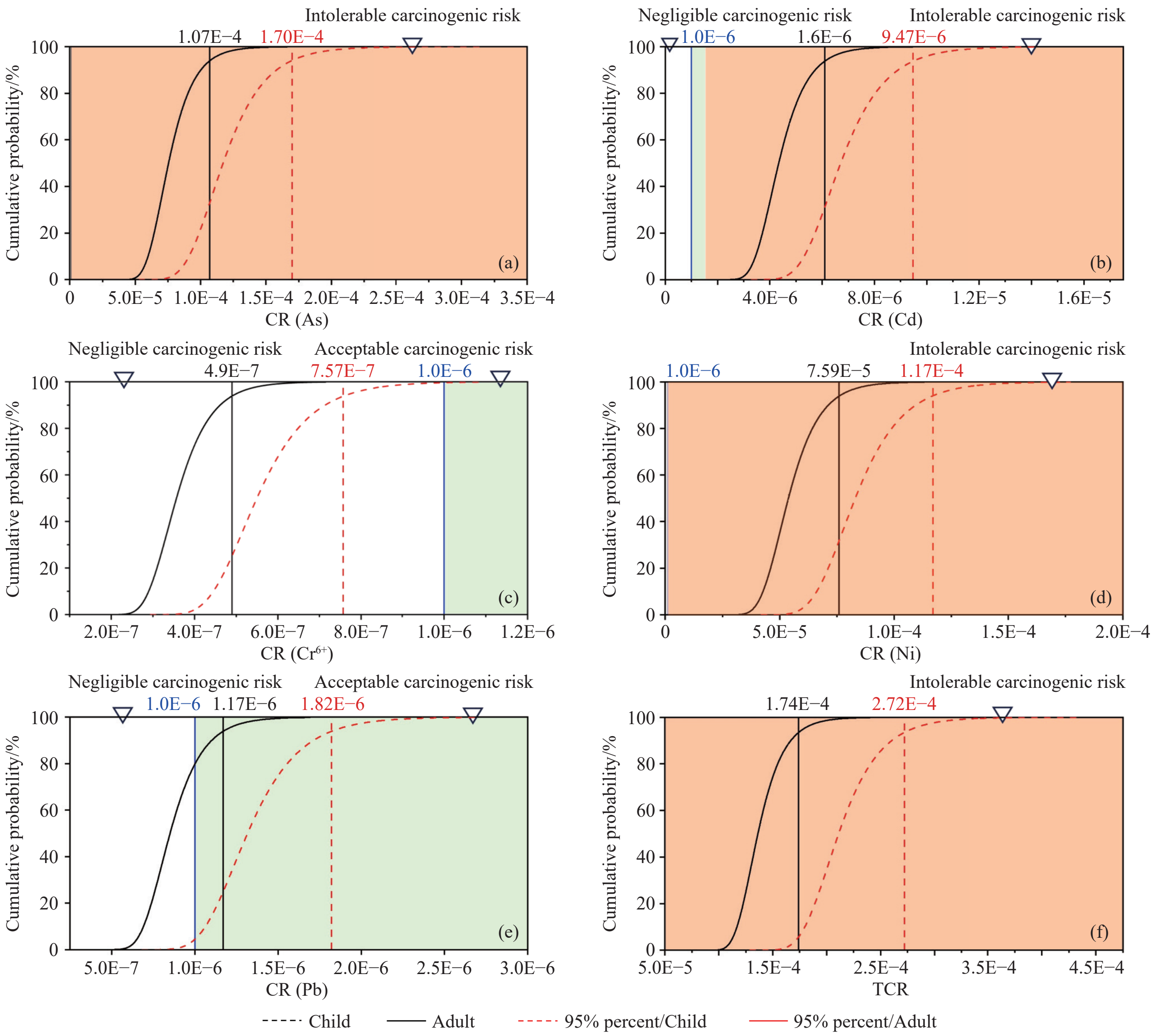

Fig. 7. Probability distribution of heavy metal carcinogenic risk in groundwater. (a) As, (b) Cd, (c) Cr, (d) Ni, (e) Pb, and (f) *TCR* for carcinogenic risk in children and adults.

the risk value, while a negative value indicates an inverse correlation (Fang Q et al., 2021). The results of the sensitivity analysis for non-carcinogenic and carcinogenic risks of groundwater around Xining City are shown in Fig. 7.

For non-carcinogenic risk, the concentrations of As, Fe, and EF (exposure frequency) are the top three factors influencing sensitivity for both children and adults. Among these, As concentration shows the highest sensitivity for both groups, followed by Fe concentration. The non-carcinogenic sensitivity of these factors is higher in children than in adults (Fig. 7a). Additionally, EF (exposure frequency) contributes 17.54% and 17.6% to the sensitivity in children and adults, respectively, also affecting non-carcinogenic risk.

Among the heavy metals, the sensitivity ranking for non-carcinogenic health risk in children and adults from highest to lowest is: As, Fe, Al, Pb, and Mn, explaining between 8.77% and 34.14% of the sensitivity. The effects of B, Ba, Sb, Zn, Cu, Cr^{6+}, Cd, Ni, and Co on non-carcinogenic sensitivity for both children and adults are negligible.

For carcinogenic risk, the concentrations of As, Ni, and *EF* (exposure frequency) explain 16.36% to 38.08% of the sensitivity in both children and adults, with significant differences in influencing factors between the two age groups. Specifically, children show higher sensitivity to carcinogenic health risks than adults (Fig. 8b).

The ranking of heavy metals affecting carcinogenic sensitivity for both children and adults from highest to lowest is As, Ni, and Cd. *BW* (body weight) and *AT* (average exposure time) also contribute to sensitivity to some extent, however, their values are negative in both non-carcinogenic and carcinogenic risk assessments. This indicates a negative correlation with risk values — as body weight and exposure time increase, the health risk decreases. This suggests that individuals with greater body weight or longer-term exposure to heavy metals in groundwater may have higher tolerance to certain pollutants or harmful substances, consistent with

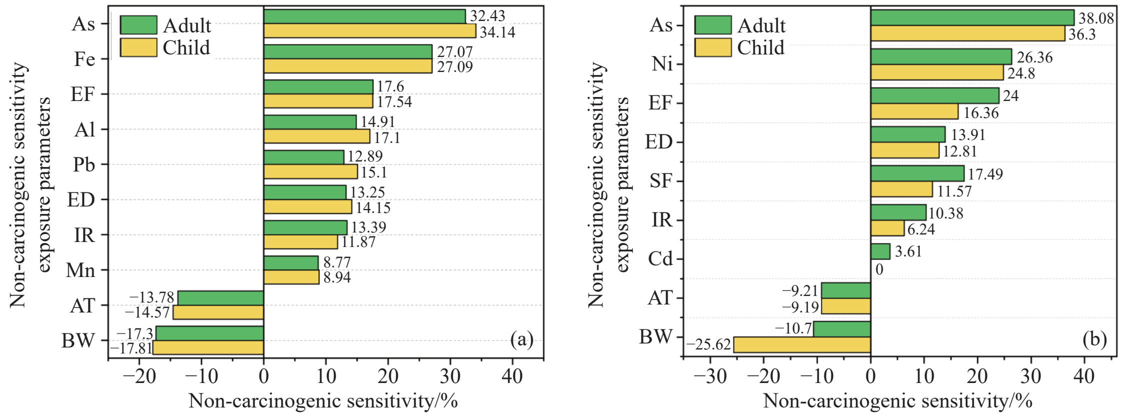

Fig. 8. Sensitivity analysis of groundwater heavy metal (a) non-carcinogenic and (b) carcinogenic risks.

previous studies (Zheng LL et al., 2025).

Currently, multiple regions have conducted non-carcinogenic and carcinogenic health risk assessments of heavy metals in groundwater, indicating significant differences in health risks caused by exposure through drinking water among various cities. At the national scale, there are considerable variations in the primary risk factors and risk levels across different regions. For example, the carcinogenic risk (*CR*) of Cr in groundwater in Urumqi exceeds 1×10^{-6}, and the *CR* of Cr^{6+} in groundwater in Tongchuan reaches as high as 8×10^{-4}, far exceeding acceptable levels (Li et al., 2024, Nsabimana et al., 2021). These results suggest that the northwest region has relatively high carcinogenic and non-carcinogenic risks associated with elements such as Cr and As, with children being a highly sensitive exposed population.

In contrast, in the North China region (e.g., Beijing), although the *CR* values of As and Cd in groundwater are high (e.g., As in Tongzhou District is 2.0×10^{-5}, and Cd in Changping District is 2.3×10^{-6}), they remain below international acceptable limits (Gao JJ et al., 2004), indicating a relatively controllable pollution risk. The South China region is characterized by complex pollution, heavy metals in Foshan groundwater are significantly affected by sediment accumulation (Huang YY et al., 2008), and the *CR* of As in Shenzhen tap water reaches 3.44×10^{-6}, approaching the threshold (Zhao JH et al., 2018).

Northwest valley cities exhibit a “As-Ni synergistic dominant” complex pollution pattern, attributed to the unique dual driving mechanisms of “non-ferrous metal smelting + valley topography pollution retention” in the northwest region, which facilitates the accumulation of metals such as As and Ni within enclosed hydrological units.

5. Conclusions

(i) In Xining City, 7 out of 14 heavy metals in groundwater exceed the Class III groundwater quality standard. The exceedance rates from highest to lowest are Al, Fe, Ba, Mn, Pb, B, As, and Ni. Their detection rates from highest to lowest are Al, Fe, B, Ba, Mn, Sb, Zn, As, Pb, Ni, Cr^{6+}, Cd, Cu, and Co. These heavy metals are mainly distributed in the valley plain area, with primary sources being natural geological background and industrial and agricultural activities. The other seven metals do not exceed the standard. The Nemero comprehensive pollution index (N_i) for Al, Pb, Mn, and Fe all exceed the clean level, indicating that the study area is severely polluted. Special attention and enhanced regulation are needed for these four heavy metals.

(ii) The health risk assessment results indicate that the carcinogenic risk of heavy metals is the primary contributor to the overall health risk. The total health risk from exposure via drinking water is higher in children than in adults. Compared to the non-carcinogenic risk of heavy metals, the carcinogenic risks of As and Ni ($HQ > 1$) are the main factors causing health risks and should be given priority attention. The risk from Cr is the lowest and its carcinogenic risk to humans can be considered negligible.

(iii) In the groundwater surrounding Xining City, concentrations of heavy metals such as As and Fe, as well as exposure frequency (*EF*), have significant impacts on the non-carcinogenic risks for both children and adults, with As showing the highest sensitivity and greater impact on children than adults. For carcinogenic risks, As, Ni, and Cd have substantial effects, with children exhibiting higher risks than adults do. Body weight (*BW*) and average exposure time (*AT*) are negatively correlated with the health risks.

CRediT authorship contribution statement

Shi-yu Liu, Bing Yi and Chun-yan Liu conceived of the present idea. Bing Yi and Chun-yan Liu carried out field investigation and sample collection. Shi-yu Liu, Bing Yi and Chun-yan Liu processed experiment data and drawed pictures. All authors discussed the results and contributed to the final manuscript.

Declaration of competing interest

The authors declare no conflicts of interest.

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