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Original Article

Health risk assessment of heavy metal pollution in groundwater of a karst basin, SW China

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Abstract: To investigate the presence of metal elements and assess their health risk for the populace in the Nandong Underground River Basin (NURB), we conducted an analysis of eleven common heavy metals in the water body. A Health risk assessment (HRA) model was employed to analyze 84 water samples from the NURB. The detection results revealed the following order of heavy metals concentrations: Fe > Al > Mn > Zn > As > Cd > Pb > Cr > Ni > Cu > Hg. Correlation analysis indicated a certain similarity in material source and migration transformation among these eleven metal elements. Our study identified that the health risks for local residents exposed to metal elements in the water of NURB primarily stem from carcinogenic risk (10^{-6}–10^{-4} a^{-1}) through the drinking water pathway. Moreover, the health risk of heavy metal exposure for children through drinking water was notably higher than for adults. The maximum health risks of Cr in both underground and surface water exceeded the recommendation standard (5.0×10^{-5} a^{-1}) from ICRP, surpassing the values recommended by the Swedish Environmental Protection Agency, the Dutch Ministry of Construction and Environment and the British Royal Society (5.0×10^{-6} a^{-1}). The results of the health risk assessment indicate that Cr in the water of NURB is the primary source of carcinogenic risk for local residents, followed by Cd and As. Consequently, it is imperative to control these three carcinogenic metals when the water was used as drinking water resource.

Keywords: Water Pollution; Correlation Analysis; Toxicity of Heavy Metal Elements; Underground River Basin; Carcinogenicity Potential

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Introduction

Heavy metals are widely distributed in various environmental contexts and possess characteristics such as persistence, carcinogenicity, biomagnification and biocondensation etc. These traits can lead to significant environmental pollution with adverse effects on human health. While some heavy metals are essential for constituting the living organism's body and promoting metabolism, they become toxic when their concentrations exceed certain thresholds (Anthony et al. 2022; Ameh et al. 2019). Representative studies, such as those by Mashaal et al. (2020) and Bakyayita et al. (2019), highlight the toxicity, carcinogenicity and potential for damage to the nervous system, liver and skin associated with arsenic exposure in water.

In a typical research, Ciner et al. observed that the widespread consumption of arsenic-contaminated water in central Turkey resulted in both children and adults being exposed to the carcinogenic

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risks associated with arsenic (Ameh et al. 2019). In China, Luo et al. (2019) conducted an assessment of the potential dispersion of elements and associated health risks related to potentially toxic elements in the soil-water-plant system at the Xiangtan manganese mine. Their findings revealed severe contamination of the tripartite system involving Mn, Cd and Pb. Importantly, it was demonstrated that these three heavy metals could be transferred from the soil-water-plant system to the human body through the food chain. Furthermore, studies have indicated that so-called non-carcinogenic metals such as Al, Mn, Cu, Fe and Zn may pose potential health risks when accumulated excessively in human bodies (Zhang et al. 2019).

The rapid development of socio-economy, industry and urbanization in recent decades had led to serious environment pollution in many countries, posing threats to public health (Sadeghi et al. 2020; Yu et al. 2022). The removal of heavy metals from industrial, agricultural, residential and environmental sources is commonly believed to increase the levels of heavy metals in water (Sadeghi et al. 2020). Both natural factors, such as topographical features, hydrogeological conditions, and geological backgrounds, and human activities, including including industrial sewage discharge, agricultural contamination and domestic litter, can influence water quality within specific regions (Adewoyin et al. 2019). Over-mining areas, Densely-populated and industrial developed areas, such as the Ota Industrial area in Ogun State, Nigeria (Susan et al. 2017) and over-mining areas have attracted significant attention due to the associated health threats to local residents (Luo et al. 2019).

The Nandong Underground River Basin (NURB), one of the four ultra-large groundwater river watersheds in Southwest China (Zhao et al. 2017), exhibits a typical karst aquifer structure and groundwater system. It has long served as a water resource for industrial, domestic and agricultural purposes. However, recent human activities have degraded the ecological environment, leading to pollution in certain water bodies and affecting water quality (Jiang et al. 2009). The unique geological structure of NURB, with high-altitude mountains in upstream recharge areas, faulted basins in midstream runoff-discharge areas, and a single groundwater drainage outlet in the low-altitude area, has been identified as contributing to harmful NO_3^- and SO_4^{2-} released from human activities, causing contamination in surface water and groundwater (Liu et al. 2023).

While the USEPA method has been widely applied by many scholars for assessing health risks in various regions, its application to evaluate heavy metal health risk in super large karst underground river basin in China, with distinct economic, physical, geographical and hydrogeological characteristics, remains unexplored. This study utilized the health risk assessment model recommended by the USEPA for hazardous substances in water to assess the health risk of 11 common heavy metals (Al, Cu, Pb, Zn, Cr, Cd, Ni, Mn, As, Fe and Hg) in the surface water and groundwater of NURB. Representative surface water and groundwater points in the watershed were selected, and samples were collected monthly from 2021 to 2022. The concentration of the 11 common heavy metals in the water samples were analyzed, and their distribution, pollution status, and dynamic change characteristics during the study period were examined. Furthermore, we used HRA model recommended by the United States Environmental Protection Agency (USEPA) to assess the health risk to local residents in NURB (USEPA, 1989; USEPA, 1992). The results of this study aim to inform policymakers about the water quality of NURB and assist in formulating scientifically sound regulations for sustainable development goals in the region.

1 Study area

The study area, the Nandong Underground River Basin, is situated in the southeast of the Yun-Gui Plateau in Yunnan Province, China (Fig. 1), lie between the latitudes 23°13'04" to 23°43'30" and longitudes 103°10'10" to 103°43'16", with the total catchments area of approximately 1,684 km^2. The climate in this region falls under the subtropical monsoon category, characterized by an annual precipitation of 830 mm and a mean air temperature of 19.8°C (Jiang et al. 2009). As of 2021, the total population in the area was around 0.45 million, with 60% residing in rural areas and actively engaged in agricultural activities. One-third of the Gross Domestic Product (GDP) was derived from agricultural output.

Due to its distinctive karst faulted basin features, the entire watershed exhibits a basin-mountain coexistence topographic feature. The geological structure is characterized by high-altitude mountains in upstream recharge areas, a series of faulted basins in midstream to runoff-discharge areas, and a significant karst development. The geological composition comprises north-south, northwest, northeast and near east-west constructions, with tertiary strata and earth-four strata mainly distribute in the

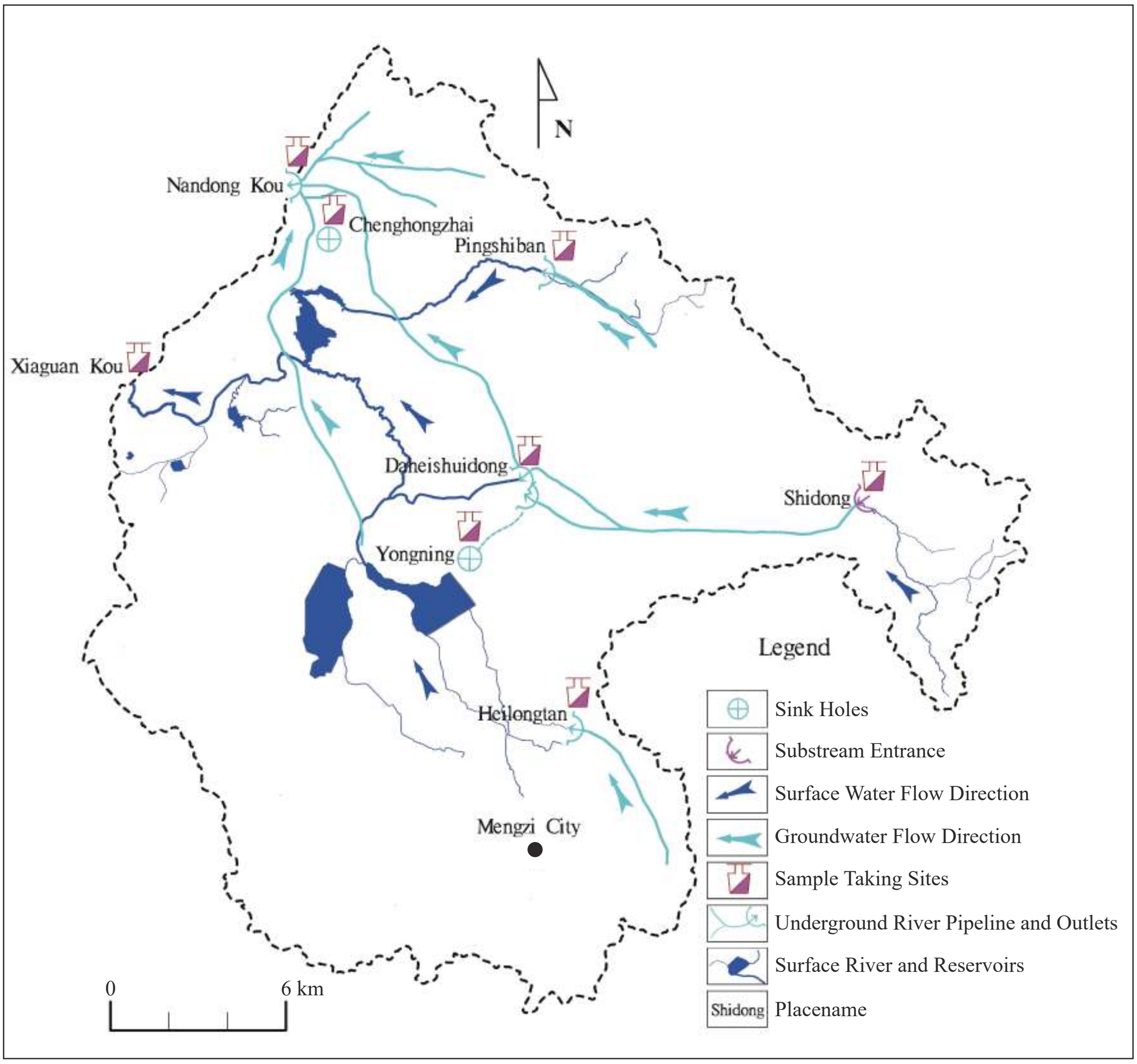

Fig. 1 Surface-underground water system of Nandong Undeground River Basin and sampling sites in our study

faulted basins. Permian limestone and white cloud limestone are widespread in the surrounding mountains, with strong karstification making them the primary aquifers. Groundwater deposits, migration, and transformation occur in the karst caves, pipelines, crannies, and other underground features within the karst areas. The Nandong Underground River is notably abundant in karst groundwater resources.

The study area's topography includes a significant elevation difference, with mountains in the upstream recharge areas reaching heights of 2,200–2,700 m, gradually descending to about 1,300 m in midstream runoff-discharge basins areas, and further lowering to 1,000 m at the outlet of Nandong underground rive. The flow of both underground and surface water originates from the surrounding mountains and converges in the basins. The surface water system is relatively underdeveloped, with only a few small rivers passing through the basin area, all merging at a single discharge point at Xiaguan Kou (Fig. 1). The groundwater outlet is situated at Nandong Kou, serving as the sole discharge point for the entire watershed. Consequently, materials released from geological backgrounds or human activities dissolve in the water, and the majority are transported to the combined outlet of surface water and groundwater. This unique hydrogeological setting provides ideal conditions for this study.

2 Samples collection and test

To comprehensive study the entire watershed, we strategically selected seven representative sampling points distributed across different locations in the NURB. These points encompassed sinkholes, substream entrances, surface river sections, and groundwater outlets, as illustrated in Fig. 1. Sampling occurred monthly from 2021 to 2022, resulting in a total of 84 samples collected throughout the year. During the water sampling process, conventional ions of water chemistry were collected in polyethylene bottles. Prior to sampling, all empty bottles were rinsed with deionized water, cleaned three times with the original sample water, and the original water samples were filtered using a 0.45 μm microporous filter before bottling.

Each group of samples, totaling 1,000 mL of water, was divided into two 500 mL sampling bottles. Additionally, 2 mL of HNO_3 (1:1) was titrated into each bottle to stabilize the heavy metals in the water. The bottles were sealed with membrane on-site and stored in a 4°C icebox for transport to the laboratory, where elements concentrations were promptly tested. On-site testing involved measuring conventional chemical indicators such as dissolved oxygen (DO), pH, oxidation-reduction potential (Eh), and electrical conductivity (EC) using a multi-parameter instrument. Concentrations of the 11 heavy metal elements in all samples were analyzed at the Karst Geology and Resources Environment Testing Center, Department of Natural Resources, China.

Specifically, Al, Cu, Pb, Zn, Cr, Cd, Ni, Mn, As and Hg were analyzed using inductively coupled plasma mass spectrometer (ICP-MS), while Fe was determined using a full universal straight read plasma spectrometer (IRIS Intrepid Ⅱ XSP). Each indicator (element) in every sample underwent three tests, and the mean values were considered as the final detection data. Test accuracy was maintained to four decimal places. Blank samples were also included as controls during the test process, ensuring that the standard deviations of all results for all samples remained below 5%.

The detection limits for the 11 heavy metal elements were as follows: Al (0.6 ug/L), Cu (0.09 ug/L), Pb (0.07 ug/L), Zn (0.8 ug/L), Cr (0.09 ug/L), Cd (0.06 ug/L), Ni (0.07 ug/L), Mn (0.06 ug/L), As (0.09 ug/L), Fe (0.005 mg/L) and Hg (0.07 ug/L), respectively.

3 Health risk assessment model

3.1 Average daily exposure dose

Typically, heavy metals enterthe human body through drinking water or skin contact, with more than 90% of pollutants entering through these pathways (Zhou et al. 2019). Metals, as common pollutants, are categorized into carcinogenic and non-carcinogenic health risks upon entering the human body. The health risk assessment model recommended by the US EPA for hazardous substances in water was employed to assess the health risks for adults and children under these two exposure models (USEPA, 1989; USEPA, 1992).

The average daily dose from exposure to metals through drinking water is defined by:

$$\mathrm{ADD}_i = \frac{C_w \cdot \mathrm{IR} \cdot \mathrm{ED} \cdot \mathrm{EF}}{\mathrm{BW} \cdot \mathrm{AT}} \tag{1}$$

The average daily dose from exposure to metals through skin contacting is defined by:

$$\mathrm{ADD}_d = \frac{C_w \cdot \mathrm{SA} \cdot \mathrm{ET} \cdot \mathrm{ED} \cdot \mathrm{EF} \cdot \mathrm{CF} \cdot \mathrm{PC}}{\mathrm{BW} \cdot \mathrm{AT}} \tag{2}$$

Where: ADD_i and ADD_d are the average daily dose per unit body weight of metal element W exposed through drinking water and skin contact, mg $(\mathrm{kg \cdot d})^{-1}$; C_w is the average concentration of the metal element W, mg·L^{-1}; IR is the average daily ingestion rate of human beings, typically set at 2.2 L·d^{-1} for adults and 1 L·d^{-1} for children (Duan et al. 2014; Duan et al. 2016); ED is the exposure duration of the metal element W, with 70 a for carcinogenic metal elements and 35 a for non-carcinogenic metal elements (Duan et al. 2014; Duan et al. 2016); EF is the exposure frequency of the metal element W, calculated at 365 d·a^{-1} (Environmental Protection Agency, 2016). BW is the body weight, with an average of 57.0 kg for adults in Yunnan, and 23.8 kg for children (Duan et al. 2014; Duan et al. 2016); AT is the average exposure time, set at 25,550 d (70 a) for carcinogenic metal elements and 12,775 d (70 a) for non-carcinogenic metal element is (Lin et al. 2020). In formula (2), SA is the contact area between water and skin, set at 18,000 cm^2 for adults and 8,000 cm^2 for children (Li et al. 2020); ET is the average daily exposure time, set at 0.633 H·d^{-1} for adults and 0.4167 H·d^{-1} for children (Duan et al. 2014; Duan et al. 2016); CF is the volume conversion factor, in mL·$(cm^3)^{-1}$. PC is the permeability coefficient of metal elements to human skin upon contact, cm·h^{-1}.

3.2 Health risk assessment

Considering that metal elements exhibit different carcinogenic intensities when exposed to the population, we conducted a health risk assessment for As, Cr, Cd as chemically carcinogenic metal elements, and Al, Cu, Pb, Zn, Fe, Ni, Mn, Hg as chemically non-carcinogenic metal elements, following guidelines from the International Agency for Research on Cancer (IARC) and the World Health Organization (WHO).

The health risk assessment formula for chemically carcinogenic metal elements in water is defined by:

$$R_n = \frac{\mathrm{ADD} \cdot \mathrm{SF}}{L} \tag{3}$$

The health risk assessment formula for chemically non-carcinogenic metal elements in water is defined by:

$$R_n = \frac{\mathrm{ADD}}{\mathrm{RfD} \cdot L} \tag{4}$$

Where: R_n is the health risk of chemically carcinogenic and non-carcinogenic metal element, expressed in a^{-1} in the water; ADD is the average daily dose per unit body weight of metal element *W* exposed through drinking water or skin contact, in mg $(kg \cdot d)^{-1}$; *SF* is the slope factor of the chemically carcinogenic metal W through drinking or skin contact, in $(kg \cdot d) \cdot mg^{-1}$. *L* is the average human lifetime, which in Yunnan residents is 70 a (Yu et al. 2022). RfD is the reference dose of daily intake of a chemically non-carcinogenic metal element W through drinking or skin contact, mg. $(kg \cdot d)^{-1}$. The parameters values of PC, SF and RfD are shown in Table 1. Data related to the population, Gross Domestic Production (GDP; core economic indicator of a region to measure a region's social-economic status), and urban development were obtained from the Luxi County statistical yearbook.

3.3 Total health risk assessment

In this study, we utilized the HRA model recommended by the United States Environmental Protection Agency (USEPA) to assess the overall health risk to humans (USEPA, 1989; USEPA, 1992). We hypothesized that the toxic effect of heavy metal elements in the water body on human health represent a cumulative impact. Therefore, the total health risk of multiple elements Rt is defined by the equation below:

$$R_t = \sum R = R_i^c + R_i^n + R_d^c + R_d^n \tag{5}$$

4 Results and discussion

4.1 Water chemistry type

The water chemical characteristics of NURB are illustrated through a Piper diagram (Fig. 2). We classified the water chemistry types according to the Shukarev classification, considering 98 water samples (including surface water and underground water) collected from NURB during the study period. From Fig. 2, it is evident that the majority of water samples fall within areas where carbonic acid hardness exceeds 50%, indicating distinctive characteristics of alkaline earth metals and weak acids in the water chemistry.

In the anion triangle diagram, all anions are concentrated in the lower left corner, with HCO_3-dominating among the anions. This dominance suggests that carbonate rock weathering is the primary source of aqueous protons. Similarly, in the cation triangle diagram, all cations are concentrated in the lower left corner, with Ca^{2+} being the predominant cation, followed by Mg^{2+}. Overall, the water chemistry types in NURB are primarily characterized as HCO_3-Ca and HCO_3-Ca·Mg, with some surface water exhibiting $HCO_3 \cdot SO_4$-Ca·Mg types.

Table 1 Values of parameters related to health risk assessment

Metal		**PC**	**SF/(kg·d)·mg^{-1}**		**RfD/mg·(kg·d)$^{-1}$**	
		(10^{-3}/cm·h^{-1})	**Drinking water**	**Skin penetration**	**Drinking water**	**Skin penetration**
Carcinogenic	As	1.8	1.5	3.66	/	/
	Cr	2	41	41	/	/
	Cd	1	6.1	6.1	/	/
Non-carcinogenic	Al	10	/	/	0.14	0.14
	Cu	0.6	/	/	0.04	0.012
	Pb	0.004	/	/	0.0014	0.00042
	Zn	0.6	/	/	0.3	0.01
	Fe	0.1	/	/	0.3	0.045
	Ni	0.1	/	/	0.02	0.0054
	Mn	0.1	/	/	0.046	0.0018
	Hg	1.8	/	/	0.0003	0.0003

Note: *No reference standard value; PC, permeability coefficient; SF, slope factor; RfD, reference daily intake.

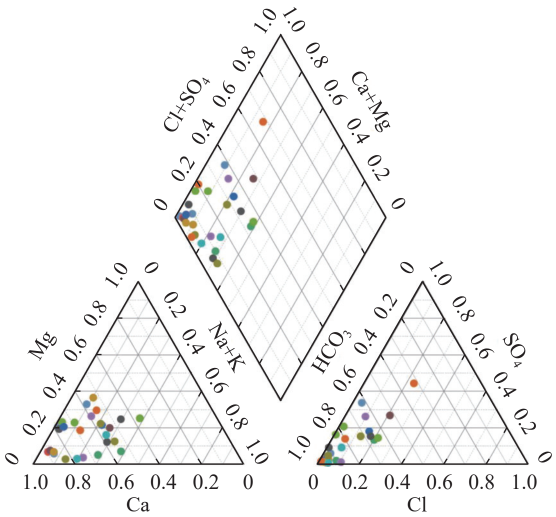

Fig. 2 Piper diagram of water samples in NURB

Based on the chemical analysis and in conjunction with previous studies in the same region (Zeng et al. 2019; Ran, 2020), we can infer that the majority of the 11 heavy metal elements studied are likely derived from the weathering of background rocks in the Earth's crust.

4.2 Concentration changes of heavy metal elements in the water

The concentrations of the 11 heavy metal elements (Al, Cu, Pb, Zn, Fe, Cr, Cd, Ni, Mn, As and Hg) are presented in Table 2. The average concentrations of these elements in the water samples from the NURB follow the order of Fe> Al >Mn >Zn> As >Cd >Pb >Cr> Ni> Cu >Hg. Notably, Fe, Al and Mn exhibit higher concentrations than the remaining eight elements, reaching the range of 10^{-2} $\mu g \cdot L^{-1}$.

Comparing these concentrations with the limit values specified for Grade Ⅲ water in the Standard for Surface Water Environmental Quality (GB 3838—2002), Standard for Groundwater Quality (GB/T 148—2017), the Standard for Drinking Water Quality (GB 5749—2006), as well as the US EPA drinking water quality standard (Lan et al. 2022; EPA, 2006), revealed that concentrations of Al, Pb, Zn, Fe, Cd, Mn, As and Hg in our water samples exceeded all three standard limitations mentioned above. The maximum concentrations of these elements exceeding the standard limitations

Table 2 Concentrations of metals in the water of Nandong Groundwater River Basin ($\mu g \cdot L^{-1}$)

Metals *n*=84	**Scope**	**Average**	**Standard deviation**	**Variation coefficient**	**Exceed standard limitation (%)**
Al	9.90–5,274.00	440.04	913.09	2.08	38.10
Cu	nd–26.70	2.34	4.75	2.03	0
Pb	nd–124.00	3.62	15.43	4.26	2.38
Zn	nd–1,311.00	82.39	211.24	2.56	1.19
Fe	nd–7,790.00	486.83	1,127.61	2.32	26.19
Cr	1.10–10.70	3.47	2.08	0.60	0
Cd	nd–61.00	3.63	10.34	2.85	7.14
Ni	0.78–13.90	2.99	2.22	0.74	0
Mn	2.44–2,035.00	113.13	276.85	2.45	15.48
As	nd–54.70	6.13	8.01	1.31	17.86
Hg	nd–0.94	0.41	0.26	0.63	40.48

Metals *n*=84	China			US EPA	WHO
	Drinking water (Limits)	Surface water（Ⅲ）	Ground water（Ⅲ）	Drinking water	Drinking water
Al	200	–	200	–	200
Cu	1,000	1,000	1,000	1,300	2,000
Pb	10	50	10	15	10
Zn	1,000	1,000	1,000	–	–
Fe	300	–	300	–	300
Cr	50	50	50	100	50
Cd	5	5	5	5	3
Ni	20	–	20	–	70
Mn	100	100	100	–	400
As	10	50	10	10	10
Hg	1	0.1	1		

*nd means not detected, –means no corresponding reference value.

reached 26.37, 12.40, 1.31, 25.97, 12.20, 20.34, 5.47 and 9.40 times of the standards, respectively.

Notably, Hg, Al and Fe are the three elements that exceeded the standard limitation the most in the research area waters, with maximum values of these three elements' concentrations exceeding the standards by more than 20 times. Therefore, special attention must be given to Hg, Al, Fe and Mn elements before utilization.

Comparing with the standards set by USEPA and WHO, most water quality index values in China are either less than or equal to the standard limits of United States and international standard. However, the standard limit for Cd (5 μg·L^{-1}) in China is higher than the WHO (3 μg·L^{-1}). Consequently, from an international perspective, Cd in the water of our study area also requires attention.

Fig. 3 illustrated the spatial distributions and dynamic changing characteristic of metal elements in surface water and groundwater throughout the months from January to December. Spatially, Zn, Cr, Cd and Ni elements in the groundwater sam-

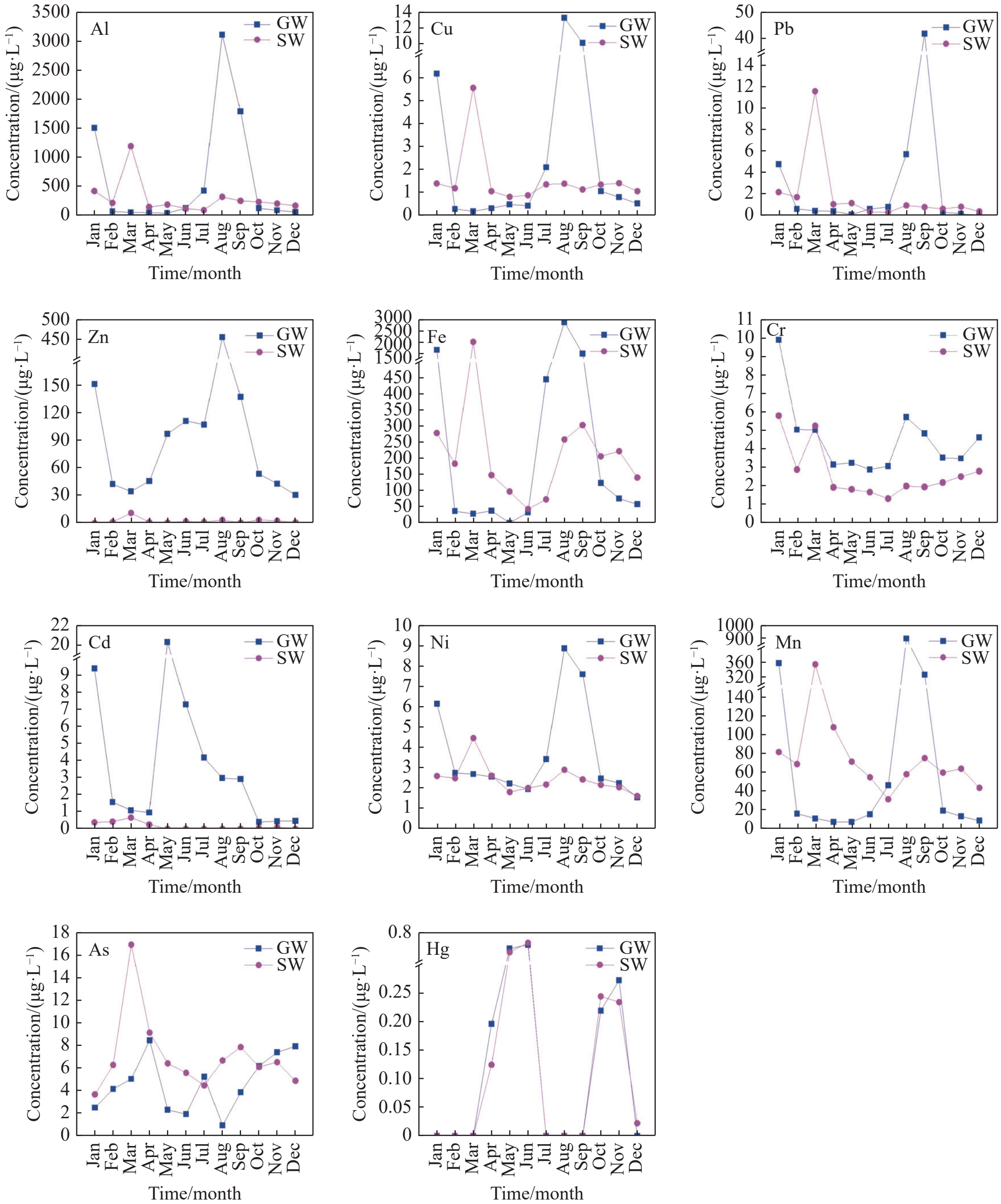

Fig. 3 Distributions and dynamic changes of metal elements in surface and groundwater samples in NURB

*GW means groundwater, SW means surface water ples generally exhibit higher concentrations than those in the surface water samples for most months during the study period, with As showing the opposite characteristic. In terms of the temporal scale, variation in element concentrations in groundwater were observed to have larger amplitudes compared to surface water.

The concentrations of Al, Cu, Pb, Zn, Fe, Cr, Ni and Hg in all water samples demonstrate similar trends in terms of temporal changes, while Zn and Cd elements exhibit an opposite changing trend. Special attention should be given to Al, Pb, Zn, Fe, Cd, Mn, As and Hg, especially during periods when they have high concentrations that exceed standard limitations. For instance, the Al element shows high concentrations from January to March in surface water and from June to September in groundwater. This information is crucial for raising awareness among local residents, prompting them to take the issue seriously and avoid potential risks when utilizing these waters.

4.3 Correlation analysis

The correlation matrix for the 11 heavy metals and pH in the water samples is presented in Table 3. As indicated in the table, none of the correlations between water pH and each element were found to be significant ($p > 0.05$). This suggests that the impact of pH on the concentration distributions of metal elements was not pronounced. The reason for this is that the pH values from the water samples in the study area ranged from 6.84–7.96, with a coefficient of variation of only 0.02, indicating minimal variation throughout the entire year.

Significant positive correlations ($p < 0.01$) were observed between Al, Cu, Pb, Fe, Cr, Ni and Mn elements. Zn exhibited significant positive correlations with Cd, Ni, Mn, Cu, and Pb at $p < 0.01$, and a significant positive correlation with Al at $p < 0.05$. As demonstrated significant positive correlation with Cu, Fe and Mn at $p < 0.01$, and a significant positive correlations with Pb at $p < 0.05$. These results suggest that these metal elements share certain similarity in terms of material source and migration transformation (Li et al. 2020).

Moreover, Hg showed significant negative correlation with Cr at $p < 0.01$ and a significant negative correlations with Ni at $p < 0.05$. This indicates that Hg exhibits distinct differences in terms of original source and migration transformation compared to Cr and Ni elements.

4.4 Health risk assessment of heavy metals in the water

Based on the concentrations of heavy metal elements in surface water and underground water in our study area, a health risk assessment model was used to calculated the annual per capita carcinogenic and non-carcinogenic health risks in the Nandong Underground River Basin (Table 4).

Health risk assessment result for drinking water: The maximum annual per capita carcinogenic risk (10^{-6}–10^{-4} a^{-1}) was higher than the non-carinogenic health risk (10^{-11}–10^{-8} a^{-1}) through drinking water. The annual total health risk for

Table 3 Pearson correlation matrix for metal elements and pH in the water samples

n=84	EC	pH	Al	Cu	Pb	Zn	Fe	Cr	Cd	Ni	Mn	As	Hg
EC	1.000	0.164	−0.042	0.083	0.031	0.177	−0.064	0.033	0.124	0.140	0.023	0.163	0.060
pH		1.000	0.045	0.040	0.134	−0.022	0.032	0.179	−0.070	0.109	0.024	−0.041	−0.147
Al			1.000	0.746**	0.579**	0.240*	0.929**	0.632**	0.037	0.916**	0.652**	0.290**	−0.201
Cu				1.000	0.756**	0.692**	0.700**	0.479**	0.171	0.805**	0.920**	0.282**	−0.172
Pb					1.000	0.285**	0.490**	0.351**	0.112	0.690**	0.486**	0.268*	−0.103
Zn						1.000	0.166	0.210	0.469**	0.327**	0.757**	0.060	0.016
Fe							1.000	0.641**	0.014	0.836**	0.659**	0.447**	−0.207
Cr								1.000	0.199	0.643**	0.431**	0.169	−0.292**
Cd									1.000	0.095	0.141	0.032	0.297**
Ni										1.000	0.657**	0.206	−0.237*
Mn											1.000	0.294**	−0.154
As												1.000	−0.014
Hg													1.000

* Significant at 0.05 level.
** Significant at 0.01 level.
EC means Electrical Conductivity

Table 4 Annual per capita health risks caused by metals in different types of water though drinking water and skin penetration, respectively (a^{-1})

Exposure way	Metals		Groundwater		Surface Water	
			Adults	Children	Adults	Children
Drinking water	Carcinogenesis	As	/–1.93×10^{-5}	/–2.30×10^{-5}	6.91×10^{-7}–4.30×10^{-5}	8.24×10^{-7}–5.12×10^{-5}
		Cr	5.11×10^{-5}–2.30×10^{-4}	6.09×10^{-5}–2.74×10^{-4}	2.36×10^{-5}–2.30×10^{-4}	2.81×10^{-5}–2.74×10^{-4}
		Cd	/–1.95×10^{-4}	/–2.32×10^{-4}	/–4.67×10^{-6}	/–5.56×10^{-6}
	No-carcinogenesis	Al	4.53×10^{-11}–1.97×10^{-8}	5.39×10^{-11}–2.35×10^{-8}	3.70×10^{-11}–1.69×10^{-8}	4.41×10^{-11}–2.01×10^{-8}
		Cu	/–3.50×10^{-10}	/–4.16×10^{-10}	2.23×10^{-12}–2.70×10^{-10}	2.65×10^{-12}–3.21×10^{-10}
		Pb	/–4.64×10^{-8}	/–5.53×10^{-8}	/–1.64×10^{-8}	/–1.95×10^{-8}
		Zn	/–2.29×10^{-9}	/–2.73×10^{-9}	/–7.67×10^{-11}	/–9.13×10^{-11}
		Fe	/–8.31×10^{-9}	/–9.90×10^{-9}	/–1.36×10^{-8}	/–1.62×10^{-8}
		Ni	3.85×10^{-11}–3.64×10^{-10}	4.59×10^{-11}–4.34×10^{-10}	2.04×10^{-11}–2.86×10^{-10}	2.43×10^{-11}–3.40×10^{-10}
		Mn	2.78×10^{-11}–2.31×10^{-8}	3.31×10^{-11}–2.76×10^{-8}	6.07×10^{-11}–1.44×10^{-8}	7.23×10^{-11}–1.72×10^{-8}
		Hg	/–1.54×10^{-9}	/–1.83×10^{-9}	/–1.64×10^{-9}	/–1.96×10^{-9}
Drinking water	Carcinogenesis	As	/–4.40×10^{-7}	/–3.37×10^{-7}	1.57×10^{-8}–9.78×10^{-7}	1.21×10^{-8}–7.49×10^{-7}
		Cr	5.30×10^{-7}–2.38×10^{-6}	4.06×10^{-7}–1.83×10^{-6}	2.45×10^{-7}–2.38×10^{-6}	1.87×10^{-7}–1.83×10^{-6}
		Cd	/–1.01×10^{-6}	/–7.74×10^{-7}	/–2.42×10^{-8}	/–1.85×10^{-8}
	No-carcinogenesis	Al	2.35×10^{-12}–1.02×10^{-9}	1.80×10^{-12}–7.83×10^{-10}	1.92×10^{-12}–8.75×10^{-10}	1.47×10^{-12}–6.71×10^{-10}
		Cu	/–3.62×10^{-12}	/–2.78×10^{-12}	2.31×10^{-14}–2.80×10^{-12}	1.77×10^{-14}–2.14×10^{-12}
		Pb	/–3.21×10^{-12}	/–2.46×10^{-12}	/–1.13×10^{-12}	/–8.68×10^{-13}
		Zn	/–2.14×10^{-10}	/–1.64×10^{-10}	/–7.15×10^{-12}	/–5.48×10^{-12}
		Fe	/–2.87×10^{-11}	/–2.19×10^{-11}	/–4.70×10^{-11}	/–3.59×10^{-11}
		Ni	7.39×10^{-14}–6.99×10^{-13}	5.66×10^{-14}–5.35×10^{-13}	3.92×10^{-14}–5.48×10^{-13}	3.00×10^{-14}–4.20×10^{-13}
		Mn	3.68×10^{-13}–3.07×10^{-10}	2.82×10^{-13}–2.35×10^{-10}	8.04×10^{-13}–1.91×10^{-10}	6.16×10^{-13}–1.46×10^{-10}
		Hg	/–1.43×10^{-11}	/–1.10^{-11}	/–1.53×10^{-11}	/–1.17×10^{-11}

"/"means no calculation results.

children was significantly higher than that for adults, mainly due to the greater sensitivity of children as risk receptors (Zhou et al. 2019; Verma et al. 2020). Similar findings were observed in the study of the Huixian Karst wetland in Guilin (Ba et al. 2022), validating the reliability of our results. The most significant carcinogenic risks were associated with Cr, Cd, and As, the concentration of which followed the order of Cr > Cd > As in groundwater and Cr > As > Cd in surface water. The carcinogenic risk caused by Cr (2.74×10^{-5}–2.30×10^{-4} a^{-1}) exceeded the maximum acceptable risk value of 5.0×10^{-5} a^{-1} stipulated by the International Commission on Radiological Protection (ICRP) for both children and adults (USEPA, 2013). Furthermore, carcinogenic risk caused by Cr from underground water is lower than surface water. Fortunately, the carcinogenic risk of Cd in surface water did not pose a significant harm to children and adult. In all water samples, the carcinogenic risk of As in the surface water that exposed to children exceed the maximum acceptable risk value of ICRP. To mitigate potential carcinogenic risks, it is essential to address Cr, Cd and As in the water before using it as the drinking water resource.

The maximum non-carcinogenic risks caused by heavy metal elements in the water were in the order of Pb > Mn > Al > Fe > Zn > Hg > Ni > Cu in underground water and Al > Pb > Mn > Fe > Hg > Ni > Cu > Zn in surface water. However, these non-carcinogenic metal elements and the total health risk were all below 5.0×10^{-5} a^{-1}. Hence, there were no potential health risks associated with non-carcinogenic metal elements in the water exposed to local residents through drinking, while carcinogenic metal elements in the water were the main source of potential health risks for the local residents through drinking.

According to the research on human heavy metal exposure in the Gejiu Tin Mining Area located in NURB and surrounding areas, Yang et al found elevated levels of As, Cd, Cr, Pb, Hg, Cu and Zn in human hair, with As being the highest (Yang et al. 2023). This highlights concerns about the health of local residents.

Health risks resulting from skin penetration: For all 11 metal elements in our study, the maximum annual per capita carcinogenic risk (10^{-8}–10^{-6} a^{-1}) was higher than non-carcinogenic health risk (10^{-13}–10^{-9} a^{-1}) through skin penetration. In contrast to the results for drinking water, the average annual total health risk caused by skin penetration was lower for children than for adults. Simultaneously, health risks for local residents exposed to metal elements in the water through skin penetration were lower than through drinking (lower by 1 to 2 orders of magnitude). Similar health risk assessment results were found in the evaluation of Huixian karst wetland in Guilin by the other scholars, supporting the validity of our assessment (Li et al. 2021； Ba et al. 2022).

The most significant health risks for residents exposed to carcinogenic metal elements were in the order of Cr > Cd > As in underground water and Cr > As > Cd in surface water. Exposure to non-carcinogenic metal elements followed the order of Al > Mn > Zn > Fe > Hg > Cu > Pb > Ni in underground water and Al > Mn > Fe > Hg > Zn > Cu > Pb > Ni in surface water. Meanwhile, the annual total carcinogenic and non-carcinogenic health risk values for residents caused by skin penetration were concentrated in the range of 10^{-6} to $10^{-13}\cdot a^{-1}$, much lower than $5.0\times10^{-5}\cdot a^{-1}$. Therefore, the 11 metal elements in water through skin penetration did not pose significant harm to local residents.

Fig. 4 and Fig. 5 depict the variations in the maximum total health risk values in different months for adults and children exposed to metal

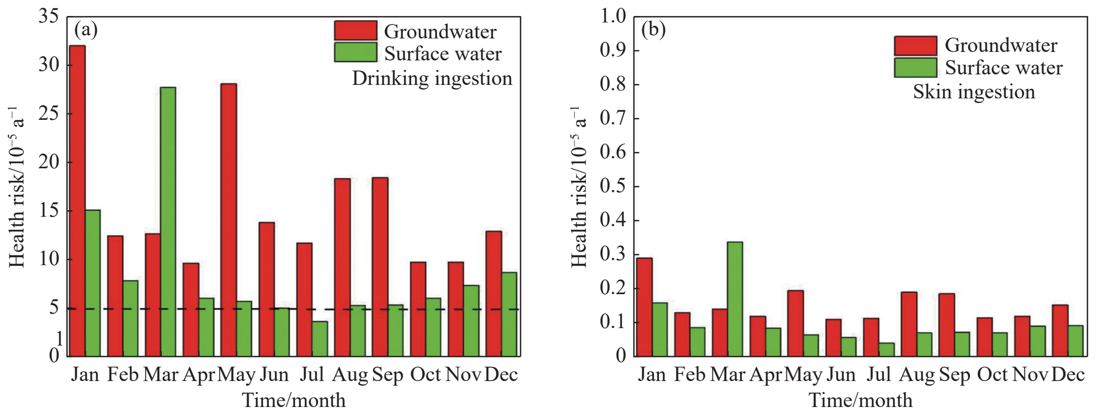

Fig. 4 Monthly maximum health risks exposure to metal elements from different water sources for adults through: (a) Drinking; (b) Skin penetration

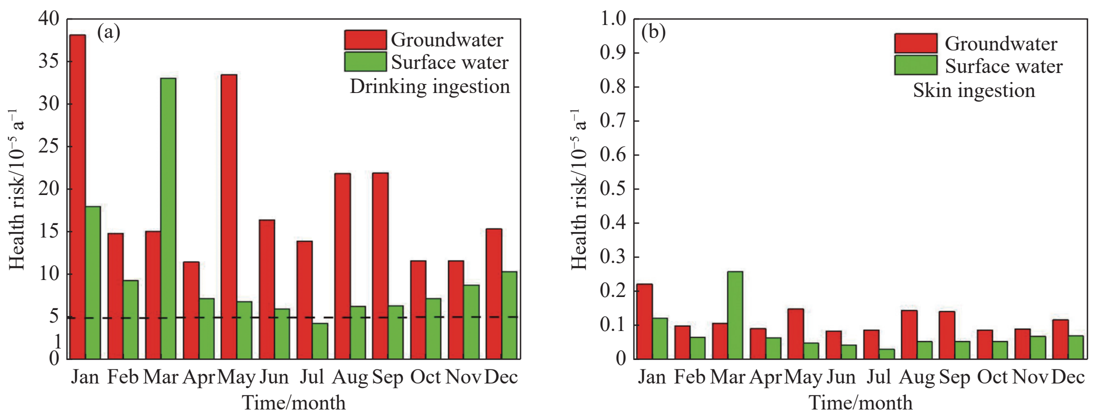

Fig. 5 Monthly maximum health risks exposure to metal elements from different water sources for children through: (a) Drinking; (b) Skin penetration

elements in the water throughout the year from 2021 to 2022. The figures indicate that the maximum health risk values for both adults and children, caused by skin penetration and drinking, follow the order of January > May > September > August > June > December > March > February > July > November > October > April in groundwater and March > January > December > February > November > April > October > May > September > August > June > July in surface water.

The fluctuating health risk values across different months in NURB highlight distinct water flow process and hydrochemical dynamic conditions between surface and underground water flow fields. Similar phenomenon has been observed in Tebessa, Algeria (Bilal et al. 2021). Except for July, the maximum health risk values for adults and children exposed to metal elements in the water through drinking were consistently higher than 5.0×10^{-5} a^{-1} throughout the other months. However, those exposed to skin penetration exhibited values lower than 5.0×10^{-6} a^{-1} and these were less than an order of magnitude below the maximum acceptable level.

Therefore, it is imperative to address carcinogenic metal elements such as Cr, Cd and As when utilizing surface and groundwater water from the Nandong Underground River Basin as drinking water resource.

In our integrated health risk study of adults and children exposed to metal elements in water across China, it was observed that health risks in most regions primarily stem from carcinogenic metal elements, particularly Cr in the water (USEPA, 1992; Li, 2020; Lan et al. 2022). In our investigation within the Nandong Underground River Basin (NURB), we identified that the main source of health risk for local residents exposed to metal elements in the water is also Cr, followed by Cd and As. This observation is primarily attributed to the higher chemical carcinogenic slope factor of these carcinogenic metal elements compared to the reference dose for the average daily intake of non-carcinogenic metal elements, indicating that carcinogenic metal elements pose a greater toxicity risk to the human body.

It is crucial to note that we employed the health risk assessment model recommended by USEPA (the United States Environmental Protection Agency) to calculate health risk of water in our study. The parameters utilized in this model are internationally standardized, and they may not perfectly align with the specific conditions of Yunnan Province. Moreover, the universal nature of exposure parameters in health risk assessment models might overlook individual differences. Additionally, the heterogeneity of the metal concentrations in the water can result in spatial and temporal variations, introducing uncertainty into the evaluation results (Lan et al. 2022).

5 Conclusions

(1) The concentrations of heavy metals in the water of NURB exhibit specific patters, with iron (Fe) having the highest content, followed by aluminum (Al), and mercury (Hg) showing the lowest content in the water samples. Maximal values for Hg, Fe, Al and Mn exceeded the standard by more than 20%, with the highest value reaching 26.37 times. Consequently, additional attention should be given to monitoring these four elements when assessing water quality in NURB.

(2) The results of the health risk assessment indicate that the carcinogenic risk for local residents exposed to heavy metals in the water of the NURB was primarily associated with drinking water. The health risks for children exposed to heavy metals through drinking water was significantly higher than those for adults, underscoring the increased vulnerability for children. The main factors that contribute to cancer risk were found to be in the order of Cr > Cd > As in groundwater and Cr > As > Cd in surface water. It is imperative to implement measures to address these three metals before water consumption to ensure public health safety.

(3) Many of the detected metals in this study exhibit significant positive correlations ($p < 0.01$) with each other. Correlation analysis revealed that most of these metals share certain similarities in material origin and migration pathways. Nevertheless, mercury (Hg) stands out with distinct original sources and migration transformations from chromium (Cr) and nickel (Ni), as indicated by their significant negative correlations with each other.

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