Characteristics, Sources and Risk Assessment of Heavy Metals in the Ganjiang River Basin, China

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Received: 17 February 2019
Accepted: 4 June 2019

Abstract

Heavy metal pollution is one of the important threats to river water quality and human health. Here, we collected surface water samples from the mainstream and tributaries in the Ganjiang River basin in January and July, 2015, in order to delineate the temporal-spatial distribution characteristics of heavy metals, identify their sources, and assess their potential risk. Compared with China’s environmental quality standards for drinking water, our results revealed that 5 heavy metals, including Fe, Al, As, Mn and Tl, exceeded the standard values and the over-standard rates were 21.62%, 16.22%, 8.11%, 4.05% and 4.05%, respectively. The concentrations of hydrochemical ions and heavy metals exhibited significant seasonal variation and spatial heterogeneity. Multivariate statistical approaches indicated that intense anthropogenic activities (mining industries and agricultural activities) were the most important sources of heavy metals in the Ganjiang River, and the upstream of the Ganjiang (in southern Jiangxi Province) and the Yuan River were the regions with the most serious pollution. Assessing health risk using the hazard index (HI) and carcinogenic risk (CR) recommended by the USEPA showed that children were more susceptible to the health risk than adults, and As was the most largest contributor leading to non-carcinogenic and carcinogenic risk to human health. Therefore, effective measures such as controls on mining wastewater and the use of pesticides and fertilizers should be taken by local government to protect aquatic ecosystems and human health.

Keywords: heavy metals, distribution characteristics, source identification, health risk assessment, Ganjiang River basin

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Introduction

River water is one of the most important sources of drinking water for humans, and its quality is vital to human health [1, 2]. However, as a result of rapid industrialization and urban expansion, lots of pollutants are discharged into rivers, causing severe deterioration of river water quality [3, 4]. Heavy metal pollution, as one of the most important threats, has aroused wide attention due to its toxicity, irreversibility and persistence [4-6]. Therefore, it is necessary to analyze the sources of heavy metal pollution and assess the potential health risks to better manage and protect water resources.

Numerous studies have shown that heavy metals are derived from different natural processes, such as bedrock weathering, soil erosion and atmospheric deposition, and intensive anthropogenic activities such as agricultural runoff, domestic sewage and mineral processing [7-9]. But the sources of heavy metals are inconsistent due to differences in regional natural environments and anthropogenic activities [10, 11]. Fortunately, multivariate statistical analysis approaches, which provide reliable means to interpret the potential heavy metal pollution sources and describe water interaction dynamics, have been widely employed in geochemical and hydrochemical pollution research [4, 12, 13]. For example, Keefe et al. [13] used those techniques to characterize the sources of pollution in three water bodies, including municipal effluent, surface water and groundwater. Varol et al. [14] found that intensive anthropogenic activities, particularly the discharge of effluents from copper mines, were responsible for heavy metal pollution in the Tigris River.

When heavy metal pollution is discharged into the river, they tend to gradually accumulate at the bottom of the river. Subsequently, sediment heavy metals will be re-released into the surface water due to environmental changes, such as sediment resuspension, reduction–oxidation reaction, etc., which will increase the heavy metals concentrations [15]. Additionally, heavy metals are gradually absorbed and biomagnified in food chains, threatening aquatic life and human health [16]. Numerous studies have reported that excessive pollution would cause hypertension, vascular disease, restrictive lung disease and other organ damage [6, 17, 18]. Given the current unfavorable situation, several powerful methods, including human health risk assessment models, heavy metal pollution index (HPI), water quality index (WQI) and entropy water quality index (EWQI) have been proposed and used to evaluate the risk of heavy metal pollution [2, 4, 6, 19]. Using HPI, Rakotondrabe et al. [12] found that the value of pollution index was larger than the acceptable value and the water quality of the Mari River was poor. Similarly, Ahmed et al. [18] showed that As had higher hazard quotient values than other elements, and children were more likely to be subjected to non-carcinogenic and carcinogenic risks than adults in Surma basin.

Ganjiang River, the largest river in Poyang Lake basin, plays an important role in providing drinking water, irrigation and fishery services for the local residents [20]. The Ganjiang River basin feeds more than 20.2 million people, and the pollution of the basin has become increasingly prominent with the acceleration of industrialization and agriculturalization processes in the past decade [21, 22]. Hu et al. [23] found that mining activities and industrial activities caused severe heavy metal pollution in the river. Moreover, Zhang et al. [24] demonstrated that local residents were susceptible to non-carcinogenic and carcinogenic risks caused by heavy metal pollution, and As was the primarily pollutant-causing risk. Nevertheless, the existing research has focused on several mainstream sites or certain river sections. There is less information about the heavy metals pollution in the whole Ganjiang River basin, which could not systematically reflect the pollution levels and sources of heavy metals. Some studies have shown that hydrochemical ions are closely related to heavy metals and can serve as important pollution indicators [2, 12]. Several studies have explored the associations between heavy metals and land use patterns or bacterial communities of the Ganjiang River basin [25, 26]. To our knowledge, there is still a lack of combined analysis of hydrochemical ions and heavy metals to explore water pollution of the Ganjiang River.

Here, we collected surface water samples from mainstream and tributaries of the Ganjiang River in January and July 2015. We aimed to delineate spatial and temporal variation characteristics of heavy metals and major hydrochemistry ions, to identify the potential pollution sources of heavy metals, and to assess their potential risk for resident drinking water. This research was expected to provide important insight into studying heavy metal pollution and watershed ecosystem protection.

Materials and Methods

Study Area

The Ganjiang River basin is the largest sub-basin of Poyang Lake basin, covering an area of 8.28×10^5 km^2, 98.45% of which belongs to Jiangxi Province (Fig. 1). In the study, the total length of the main river channel is approximately 823 km. Controlled by the typical subtropical monsoon climate, the annual average temperature in the region is 18.3°C, with the hottest and coldest months being July and January, respectively. The average annual precipitation is around 1,580 mm, and heavy rainfall occurs from March to August, accounting for 72.8% of the annual precipitation.

Geologically, the study area is located on the southeastern edge of the Eurasian plate. The north and south are divided into the Yangtze block and the
Huaxia block. Magmatic activities are frequent in the basin, and magmatic rocks are widely distributed. The most widely exposed aquifers in this area are weakly water-rich magmatic rocks, metamorphic rocks, general clastic rock type aquifers, pore fissure aquifers, residual slopes, and alluvial deposits covering an area of $1.40 \times 10^5$ km$^2$, accounting for 83.2% of the province’s total area. Strong and rich water-rich karst aquifers and alluvial, lake sediment loose rock pore aquifers, with an area of $2.7 \times 10^4$ km$^2$, account for 16% of the province’s area. The hydrogeological map of the study area can be obtained from the following website: http://www.ngac.org.cn/Document/Map.aspx?MapId=EC7E1A7A79181954E0430100007F182E. The southern part of the Ganjiang River basin (southern Jiangxi Province) is abundant in tungsten ore and the output accounts for nearly a half in China [27, 28], while Chinese output accounted for 82% of the global totals [29]. Apart from tungsten, the study area is also abundant in Mn, Fe, Sn, V, U and coal mines.

Sample Collection

Two water sample surveys were conducted from the river in 37 sites along the Ganjiang River basin from its origin to mouth during dry (January 2015) and wet (July 2015) seasons (Fig. 1). Among the 37 sampling sites, 14 sites were along the mainstream, and the other were on the major tributaries. Water samples were collected from a depth of approximately 50 cm in the center of the river channel and filtered through 0.45 μm Millipore nitrocellulose filter. During sample collection, electrical conductivity (EC) was determined using a HI 98360 probe (Hanna Instruments Ltd., Italy) and HCO$_3$ was measured by titration, which were listed in Table 1. About 25 mL filtrate was acidified to pH<2 with ultra-purified HNO$_3$ in pre-cleaned high-density polyethylene bottles for metal analysis, and the remaining samples were placed into a polypropylene sampling bottles for determining hydrochemical ions. All samples were stored in a refrigerator at 4ºC in the dark until analysis.

The concentrations of major cations, including Na$^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$, were measured by a plasma emission spectrometer (Optima 8000, PerkinElmer, USA) and major anions including Cl$^-$ and SO$_4^{2-}$ were determined by ion chromatograph (ICP-90, Dionex, USA). The results of recovery percentage were between 95-100% with 2% standard deviation, and the charge balances of those cations and anions were less than 10% – verifying the precision of the measurement. The concentrations of 16 elements, including Al, Tl, V, Cr, Mn, Fe, Pb, Co, Ni, Cu, Zn, As, Mo, Cd, Sb and U were determined using ICP-MS (Thermo X series II, USA). The accuracy and precision of the methods and results were checked by using the certified Standard Reference Materials (SRM-1640 and SRM-1643e of National Institute of Scientific & Technology, USA). The detection limits were 0.065 (Al), 0.04 (V), 0.019 (Cr), 0.011 (Mn), 1.929 (Fe), 0.005 (Co), 0.044 (Ni), 0.042 (Cu), 0.027 (Zn), 0.094 (As), 0.003 (Mo), 0.001 (Cd), 0.004 (Sb), 0.004 (Tl), 0.002 (Pb) and 0.001 (U). Recovery rates of the above elements spiked in water ranged from 89% to 110%. The reagents and procedural blanks were examined in parallel using the same procedure as the sample processing. Each calibration curve was estimated by determining quality control criteria before, during, and after a set of sample measurements. The relative standard deviation (RSD) of all two-time parallel samples for all elements was less than 10%.

Data Statistical Methods

Multivariate Statistical Approaches

Multivariate statistical approaches, such as factor/principal component analysis (FA/PCA), correlation analysis, hierarchical cluster analysis (HCA) and analysis of variance (ANOVA), which can interpret underlying structures between variables and reduce dimensionality of complex datasets without much information loss, have been broadly applied to environmental pollution research [4, 12, 30]. In this study, sampling sites were grouped by HCA (Ward method) based on heavy metal data to analyse the spatial difference. ANOVA was used to test whether there were significant differences in hydrochemical parameters between different
seasons (dry season and wet season) and different zones clustered by HCA (p<0.05, least-significance difference, LSD). Pearson’s correlation heatmap was used to demonstrate associations between the selected parameters. FA/PCA (Varimax Kaiser Normalization) was conducted to identify major pollution sources, and those PCs with eigenvalue >1 were retained. Detailed statistical analysis procedures were shown in Bu et al. [31], and all statistical analyses were performed by SPSS 24.0 and Origin 2018 for Windows software packages.

Heavy Metal Pollution Index (HPI)

Heavy metal pollution index (HPI) was used to evaluate the combined effects of each heavy metal on the total quality of water [32]. The method assigns a respective weightage value (Wi) to each metal on which the index is based. The weightage value (Wi) is any value between 0 and 1, which reflects the relative importance of each metal. It can be defined as inversely proportional to the recommended standard (Si) for each parameter. In the present study, the maximum permissible value (Si) for each metal is taken from drinking water quality standard [33, 34]. The HPI model is proposed by Mohan [35]. If the HPI is below 100, the overall condition of the water body is considered to be at an acceptable level for an aquatic ecosystem [12].

\[
HPI = \frac{\sum_{i=1}^{n} Wi \cdot Q_i}{\sum_{i=1}^{n} Wi}
\]

(1)

…where Wi is the united weightage of ith parameters, Qi is the sub index of the ith parameter, and n is the number of parameters considered.

\[
Q_i = 100 \times \frac{V_i}{S_i}
\]

(2)

…where Vi and Si are the monitored concentrations in μg/L and the maximum permissible value of the ith corresponding metal, respectively.

Human Health Risk Assessment

Heavy metals pose a carcinogenic and non-carcinogenic risk to human health through two of the most common exposure pathways, including ingestion and skin absorption (excluding inhalation via the mouth and nose) [10]. The doses through oral intake and dermal pathways are calculated by Eqs. (1) and (2) respectively as below:

\[
ADD_{\text{ingestion}} = \frac{C_w \times IR \times ABS_{GI} \times EF \times ED}{BW \times AT}
\]

(1)

\[
ADD_{\text{dermal}} = \frac{C_w \times K_p \times SA \times ED \times EF \times ET \times CF}{BW \times AT}
\]

(2)

…where ADD_{\text{ingestion}} and ADD_{\text{dermal}} refer to the average daily doses from ingestion and dermal absorption respectively, and unit in μg/(kg·day); C_w, chemical concentration of heavy metals in each water sample, and are given as μg/L; IR, the ingestion rate (1.5 and 2.2 L/day for children and adults); EF is exposure frequency and equal to 350, and unit in days/year; ED, the exposure duration (6 and 30 years for children and adults, respectively); BW, the body weight (15 kg for children and 70 kg for adults); AT is averaging time (days); SA is exposed skin area (6,600 cm² for children and 18,000 cm² for adults); ET is exposure time, unit in h/day; K_p, the dermal permeability coefficient in water (cm/h); and ABS_{GI} refers to gastrointestinal absorption factor (dimensionless). The parameter values we referred to are mainly based on those proposed by the U.S. EPA [36], and some parameter values are supplemented and modified according to other references [4, 37].

Carcinogenic and non-carcinogenic risk can be quantified by calculating hazard quotient (HQ) and cancer risk (CR). HQ is evaluated by calculating the ratio of the ADD value of each exposure route (ingestion, skin) to the corresponding reference dose (RfD) to reflect the non-carcinogenic risk (Eq. (3)). When the value of HQ>1, non-carcinogenic risks should be of concern. Total hazard index (HI), the sum of the HQs, is employed to evaluate the total potential non-carcinogenic risks, with HI>1, indicating an adverse effect on human health (Eq. (5)). CR is calculated by Eq. (6), and the acceptable range is 10⁻⁶ to 10⁻⁴ [36].

\[
\text{Hazard Quotient(HQ)} = \frac{ADD}{RFD}
\]

(3)

\[
RFD_{\text{dermal}} = RFD \times ABC_{GI}
\]

(4)

\[
HI = \sum_{i=1}^{n} (HQ_{\text{ingestion}} + HQ_{\text{dermal}})
\]

(5)

\[
Cancer Risk(CR) = ADD \times CSF(cancer slope factor)
\]

(6)

Unless otherwise stated, the above models are obtained from U.S. Environmental Protection Agency documents (https://www.epa.gov/ground-water-and-drinking-water).

Results

Temporal-Spatial Variation of Major Hydrochemical Ions

The temporal-spatial variations of major hydrochemical ions from two seasons at the 37 sampling sites are shown in Fig. S1 and Table 1. ANOVA indicated little difference for each variable between mainstream and tributaries except for Cl⁻, whose average concentration in the mainstream was significantly higher than in tributaries (p = 0.014). Hydrochemical ion concentrations (except for NO₃⁻) in the dry season were significantly higher than those in the wet season.
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Temporal-Spatial Variation of Heavy Metals

The descriptive statistics of heavy metals in water samples from the Ganjiang River basin are presented in Table 2. Fe, Al and Mn were the most abundant metals in the river water, whereas Cd, Co and Tl were less abundant. Compared with China’s environmental quality standards for drinking water [33], the average concentrations of 16 heavy metals were lower than the standards. However, there were 5 heavy metals in some samples whose concentrations were higher than standard values, including Fe (16 samples), Al (12 samples), As (6 samples), Mn (3 samples), and Tl (3 samples), and the over-standard rates were 21.62%, 16.22%, 8.11%, 4.05% and 4.05%, respectively (Fig. S2).

ANOVA showed that most heavy metal concentrations (except for Cr, Zn, Mo, Sb and Tl) were significantly higher in the dry season than in the wet season (Table 2). Based on HCA (Fig. S3), 37 sampling sites were categorized into four zones (Fig. S4), including C1 (midstream of Ganjiang River), C2 (Tao River, Zhang River, Shangyou River and the downstream of Yuan River), C3 (the source of Ganjiang River, Xiang River, Gu River, Shu River, Jin River and the upstream and midstream of Yuan River), and C4 (Ping River, Mei River, Qin River, Shuihuan River, He River and Lu River). Except for the metal of Al, the average concentrations of other metals in different zones have significant differences (Table 2). The average concentrations of Mn, Co, Zn, As, Mo, Cd, Sb, Tl, Pb and U in the C2 were higher than those in others regions, while the average concentrations of V, Cr, Fe and Cu in the C3 were higher than those in others regions. Compared with others regions, the average concentrations of all the metals in C4 were lowest, indicating that water quality was relatively safe.

Risk Assessment

Heavy Metal Pollution Index

The HPI values ranged from 10.13 (Z21, wet season) to 151.76 (Z9, wet season) (Fig. 2). All sampling sites except Z9 in the wet season and Z30 in both seasons were lower than the critical pollution index limit of 100. The average HPI value in the dry season (44.97) was similar to that in the wet season (40.01), which was lower than the acceptable value (100), indicating that the surface water was generally clean as a whole and could not pose a serious threat to aquatic life and human beings in the Ganjiang River basin.

Risk Assessment on Human Health

The HQ and HI values for heavy metals via ingestion and dermal pathways for children and adults in different seasons are presented in Table S1. Both in the dry and wet seasons, the HQ_{dermal} values of all metals

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### Table 1. Descriptive statistics of hydrochemical ions in water samples from Ganjiang River basin.

|                      | EC (μS/cm) | HCO₃⁻ (mg/L) | Cl⁻ (mg/L) | SO₄²⁻ (mg/L) | Na⁺ (mg/L) | K⁺ (mg/L) | Mg²⁺ (mg/L) | Ca²⁺ (mg/L) | NH₄⁺-N (mg/L) | NO₃⁻ (mg/L) |
|----------------------|------------|--------------|------------|--------------|------------|-----------|-------------|-------------|---------------|-------------|
| **Dry season (n = 37)** |            |              |            |              |            |           |             |             |               |             |
| Min                  | 56.80      | 17.08        | 0.53       | 2.42         | 2.84       | 2.51      | 1.12        | 6.86        | 0.14          | 0.11        |
| Max                  | 241.00     | 106.55       | 57.96      | 34.29        | 44.07      | 5.48      | 6.45        | 43.06       | 1.54          | 4.26        |
| Mean                 | 127.94⁺    | 51.81⁺       | 12.64⁺     | 15.31⁺       | 17.28⁺     | 3.80⁺     | 3.36⁺       | 19.18⁺      | 0.54⁺         | 0.75⁺        |
| S.D                  | 44.12      | 23.84        | 11.62      | 8.40         | 8.05       | 0.82      | 1.34        | 9.36        | 0.33          | 0.85        |
| **Wet season (n = 37)** |            |              |            |              |            |           |             |             |               |             |
| Min                  | 32.20      | 14.64        | 1.03       | 1.50         | 0.31       | 0.73      | 0.36        | 4.49        | 0.08          | 0.51        |
| Max                  | 157.20     | 87.23        | 27.66      | 28.98        | 18.30      | 3.37      | 4.25        | 33.92       | 0.53          | 18.88       |
| Mean                 | 72.63⁺     | 36.40⁺       | 5.85⁺      | 8.87⁺        | 4.10⁺      | 1.99⁺     | 1.71⁺       | 11.87⁺      | 0.25⁺         | 3.29⁺        |
| S.D                  | 30.56      | 18.36        | 5.33       | 5.95         | 3.14       | 0.66      | 1.06        | 6.93        | 0.11          | 3.76        |
| **Mainstream (n = 14)** |            |              |            |              |            |           |             |             |               |             |
| Min                  | 48.50      | 20.13        | 2.57       | 4.57         | 1.75       | 1.42      | 0.57        | 6.30        | 0.10          | 0.29        |
| Max                  | 176.10     | 87.43        | 36.32      | 20.30        | 30.98      | 5.40      | 3.89        | 25.31       | 1.54          | 5.49        |
| Mean                 | 96.26      | 40.74        | 10.97⁺     | 11.05        | 9.37       | 3.06      | 2.25        | 13.77       | 0.43          | 1.64        |
| S.D                  | 38.36      | 15.04        | 8.15       | 4.80         | 7.24       | 1.12      | 1.01        | 4.80        | 0.32          | 1.35        |
| **Tributary (n = 23)** |            |              |            |              |            |           |             |             |               |             |
| Min                  | 32.20      | 14.64        | 0.53       | 1.50         | 0.31       | 0.73      | 0.36        | 4.49        | 0.08          | 0.11        |
| Max                  | 241.00     | 106.55       | 57.96      | 34.29        | 44.07      | 5.48      | 6.45        | 43.06       | 1.49          | 18.88       |
| Mean                 | 102.73     | 46.15        | 8.19⁺      | 12.73        | 7.88       | 2.79      | 2.71        | 16.60       | 0.37          | 2.25        |
| S.D                  | 51.61      | 25.98        | 10.34      | 9.32         | 7.64       | 1.20      | 1.66        | 10.65       | 0.26          | 3.65        |

*Different letters indicate significant differences (one-way ANOVA, LSD test, p<0.05).
|                | Al   | V    | Cr   | Mn   | Fe   | Co   | Ni   | Cu   | Zn   | As   | Mo   | Cd   | Sb   | Tl   | Pb   | U   |
|----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|-----|
| **Dry season** |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |    |
| Min            | 18.87| 0.35 | 2.93 | 4.33 | 153.20| 0.09 | 0.77 | 1.37 | 2.51 | 0.39 | 0.13 | 0.01 | 0.07 | 0.01 | 0.29 | 0.05|
| Max            | 989.70| 3.97 | 6.44 | 216.40| 1918.00| 0.54 | 8.11 | 22.13| 23.78| 97.89| 28.91| 2.67 | 0.81 | 0.13 | 3.64 | 1.00|
| Mean           | 186.94 | 1.23 | 4.69 | 336.16| 2.20 | 0.23 | 2.20 | 4.12 | 8.12 | 8.24 | 3.72 | 0.28 | 0.05 | 0.99 | 0.37 |    |
| S.D            | 186.24 | 0.78 | 0.52 | 39.02 | 1.86 | 0.11 | 4.57 | 4.52 | 19.50| 6.63 | 0.53 | 0.17 | 0.03 | 0.76 | 0.24 |    |
| **Min**        | 6.04 | 0.22 | 3.93 | 0.91 | 53.20 | 0.04 | 0.51 | 0.96 | 2.35 | 0.26 | 0.08 | 0.00 | 0.04 | 0.18 | 0.01 |    |
| **Max**        | 24.34 | 2.12 | 8.86 | 220.20| 269.40| 0.23 | 3.89 | 5.21 | 27.88| 36.09| 17.76| 4.39 | 0.16 | 3.25 | 0.38 |    |
| **Mean**       | 11.49 | 0.81 | 4.78 | 106.13| 0.08 | 1.36 | 1.99 | 7.10 | 2.99 | 1.97 | 0.14 | 0.28 | 0.04 | 0.67 | 0.08 |    |
| **S.D**        | 3.68 | 0.46 | 0.81 | 37.36 | 0.10 | 2.39 | 1.19 | 5.46 | 6.07 | 3.72 | 0.30 | 0.03 | 0.08 | 0.69 | 0.10 |    |
| **C1**         |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |    |
| Min            | 8.40 | 0.47 | 2.93 | 0.91 | 57.36 | 0.05 | 0.87 | 1.19 | 3.43 | 1.07 | 0.97 | 0.04 | 0.08 | 0.18 | 0.02 |    |
| Max            | 103.90| 3.55 | 15.42 | 195.40| 100.00| 0.36 | 8.11 | 3.60 | 10.00| 7.64 | 10.76| 1.88 | 0.32 | 0.09 | 1.27 | 0.27|
| Mean           | 39.32 | 1.10 | 4.40 | 128.28| 0.14 | 3.06 | 2.24 | 6.13 | 3.70 | 4.10 | 0.43 | 0.16 | 0.22 | 0.06 | 0.44 | 0.12|
| S.D            | 33.24 | 0.90 | 0.57 | 48.51 | 0.10 | 2.39 | 0.72 | 1.89 | 2.53 | 3.49 | 0.59 | 0.08 | 0.03 | 0.31 | 0.10 |    |
| **Min**        | 6.04 | 0.60 | 3.93 | 1.87 | 76.79 | 0.06 | 0.62 | 1.82 | 4.70 | 0.63 | 0.59 | 0.03 | 0.11 | 0.04 | 0.30 | 0.05|
| **Max**        | 371.70| 2.00 | 5.21 | 220.20| 455.80| 0.54 | 3.89 | 6.61 | 27.88| 97.89| 28.91| 2.67 | 4.39 | 0.16 | 3.24 | 1.00|
| **Mean**       | 138.35 | 1.09 | 4.64 | 251.83| 0.25 | 1.88 | 3.58 | 14.27 | 23.19 | 10.02 | 0.60 | 0.74 | 0.08 | 1.09 | 0.39 |    |
| **S.D**        | 32.34 | 0.90 | 0.57 | 48.51 | 0.10 | 2.39 | 0.72 | 1.89 | 2.53 | 3.49 | 0.59 | 0.08 | 0.03 | 0.31 | 0.10 |    |
| **C2**         |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |    |
| Min            | 7.15 | 0.22 | 4.22 | 1.24 | 70.88 | 0.04 | 0.63 | 1.23 | 2.35 | 0.46 | 0.08 | 0.00 | 0.08 | 0.01 | 0.18 | 0.01|
| Max            | 989.70| 3.97 | 8.86 | 100.50| 1918.00| 0.44 | 7.03 | 22.13| 13.35| 7.45 | 4.91 | 0.48 | 0.81 | 0.10 | 3.25 | 0.82|
| Mean           | 128.17 | 1.29 | 5.04 | 310.32| 0.19 | 2.01 | 4.49 | 7.57 | 2.14 | 1.16 | 0.11 | 0.23 | 0.04 | 0.91 | 0.27 |    |
| S.D            | 212.75 | 0.81 | 0.85 | 23.80 | 0.11 | 1.55 | 5.38 | 3.26 | 1.79 | 1.18 | 0.12 | 0.14 | 0.02 | 0.72 | 0.26 |    |
| **Min**        | 7.00 | 0.32 | 3.94 | 1.65 | 53.20 | 0.04 | 0.51 | 0.96 | 2.51 | 0.26 | 0.18 | 0.01 | 0.04 | 0.01 | 0.19 | 0.01|
| **Max**        | 553.70| 1.85 | 6.44 | 216.40| 410.70| 0.28 | 1.50 | 3.27 | 11.71| 6.26 | 1.65 | 0.10 | 0.32 | 0.07 | 3.64 | 0.60|
| **Mean**       | 75.23 | 0.70 | 4.61 | 176.60| 0.10 | 1.01 | 1.72 | 4.97 | 1.71 | 0.73 | 0.05 | 0.13 | 0.03 | 0.78 | 0.14 |    |
| **S.D**        | 117.86 | 0.33 | 0.51 | 41.93 | 0.06 | 0.27 | 0.57 | 2.04 | 1.81 | 0.43 | 0.02 | 0.06 | 0.01 | 0.80 | 0.14 |    |
| **WHOa**       | 900 | 50 | 400 | - | 70 | 2000 | 3000 | 10 | - | 3 | 20 | - | 10 | 30 |    |
| **Water quality standardb** | 200 | 50 | 100 | 300 | 70 | 1000 | 1000 | 10 | 70 | 5 | 5 | 0.1 | 10 | - |    |

*Different letters indicate significant differences (one-way ANOVA, LSD test, p < 0.05).
S.D, standard deviation; CV, coefficient of variation.
a. Guidelines for drinking water quality, fourth edition, 2011.
b. Chinese drinking water standards (GB 5749-2006).
for adults and children were smaller than 1, showing that these metals presented little hazard through dermal absorption. Similarly, in the wet season the HQ ingestion values of all metals for adults and children were below 1. However, in the dry season the HQ ingestion value of As for children exceeded 1, indicating that daily oral ingestion of As may pose a health risk.

Fig. 2. Heavy metal pollution index for different seasons at 37 sites along the Ganjiang River basin with the limit value of pollution (the dotted line).

Fig. 3. Hazard index of the mixed heavy metals in the surface water from Ganjiang River basin.
intake was the main pathway that pose potential non-carcinogenic risks.

The HI values of heavy metals between 37 sampling sites in both seasons for adults and children are shown in Fig. 3. In the dry season, the HI values of 7 sites for adults and 26 sites for children were more than 1. In the wet season, 3 sites for adults and 14 sites for children were where HI values exceeded 1. Among them, the HI values of Z12, Z13, Z14 and G16 in the dry season and Z12, Z13 and Z14 in the wet season were obviously higher than the reference value. Compared with adults, higher HI values and the over-standard rates were observed for children, indicating that the children are more sensitive to heavy metal pollution in water. In general, the As and Tl was the main contributor among HI values in both seasons. For adults, the HI values of As at Z12, Z13, Z14 and Z16 in dry season and at Z13 and Z14 in the wet season exceeded 1. For children, the HI values of As at Z10, Z12, Z13, Z14, Z15, G16, G17, G20, Z22, Z24, G26, G27, Z30, G31 and G34 in the dry season and at Z12, Z13, Z14, Z15, Z22, Z30 and Z32 in the wet season exceeded 1, and the Tl at Z30 in the dry season and at Z9 and Z30 in the wet season also exceeded 1, although it has low concentrations in the water. Therefore, we concluded that As was the largest contributor to adverse effects among the selected elements in this study.

Carcinogenic risks were calculated for Cr, Pb and As because of the lack of values of CSFs for other elements. Carcinogenic risks are presented in Table S2 and Fig. 4. Similar to HQ values, the CR_{ingestion} and CR_{dermal} values of Cr and Pb were relatively smaller compared with the reference value, indicating that Cr and Pb in water posed a minimal hazard to local residents. However, the CR_{total} value of Cr at G3 in wet season for children exceeded 1.0E-4, posing a hazard to local inhabitants. Similarly, CR_{ingestion} values of As also exceeded the acceptable value. For adults, 18 sites (dry season) and 9 sites (wet season) of the CR values exceeded 1.0E-4, which have carcinogenic effects on the health of adults. For children, 30 sites (dry season) and 28 sites (wet season) of the CR values exceeded the reference value, indicating that it posed more adverse threats to children than adults.
Relationship between Physico-Chemical Parameters

Correlation Analysis

Fig. 5 shows a correlation heatmap about heavy metals and hydrochemical ions. There were significant positive correlations among U, EC, HCO$_3^-$, Cl$^-$, SO$_4^{2-}$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, NH$_4^+/-$N, Fe, Co, Mn and Ni, except between Mn and HCO$_3^-$, Fe and Mo, Ni and Pb. Cr had no significant correlation with other parameters. NO$_3^-$ had no significant relationship with other parameters as it had significant negative correlation with Al, Fe and U.

Principle Component Analysis

The results of FA/PCA are listed in Table 3. The Kaisere-Meyere-Olkin (KMO) measure was 0.827 and the significance of Bartlett’s test was 0.000, indicating that the PCA result was effective. Six principle components with eigenvalues exceeding 1 were extracted, accounting for 79.93% of the total variance. PC1, accounting for 21.48% of the total variance, was made up of strong positive loadings on HCO$_3^-$, Ca$^{2+}$, Mg$^{2+}$, U, EC, SO$_4^{2-}$ and Fe. PC2 had 16% of the total variance with strong positive correlation to Cl$^-$, Na$^+$, K$^+$, V, K, Tl and Cu. PC3 explained 14.77% of the total variance and was comprised of Zn, Cd, Mn, Ni, Co and NH$_4^+/-$N with high loading. PC4 explained 11.82% of the total variance and was comprised of NO$_3^-$, Al and Fe with high loadings. PC5 contributed to 10.87% of the total variance and was dominated by Mo, As and Sb. PC6 consisted of Cr and Pb and accounted for 4.98% of the total variance.

As seen in Fig. S5, sites G1, Z2, G3, Z9, Z10, G11, Z12, Z13, Z14, G16, Z29, Z30, G31, Z32, Z33 and G35 in the dry season had higher correlations and contributions to PC1, corresponding to higher heavy metals and ion concentrations at these sites. However, sites Z5, Z6, Z7, G11, G17, Z18, G20, Z21, Z23, Z25 and G26 in the wet season had the opposite direction to PC1, corresponding to lower concentrations of heavy metals and ions at these sites. The above results also indicated that heavy metals were influenced by human activities and natural processes, with the dry season being more affected. The relationships between heavy metals and hydrochemical ions in the Ganjiang River basin are detailed in Table 3. The table shows the rotated component matrix of PCA on datasets of heavy metals and hydrochemical ions in the Ganjiang River basin.

Table 3. Rotated component matrix of PCA on datasets of heavy metals and hydrochemical ions in the Ganjiang River basin.

| Elements     | PC1  | PC2  | PC3  | PC4  | PC5  | PC6  |
|--------------|------|------|------|------|------|------|
| Al           | 0.23 | 0.32 | 0.23 | 0.81 | 0.06 | 0.14 |
| V            | 0.38 | 0.66 | 0.05 | 0.04 | 0.18 | 0.24 |
| Cr           | 0.00 | 0.09 | -0.01| -0.10| -0.13| 0.76 |
| Mn           | 0.22 | 0.25 | 0.66 | 0.25 | 0.07 | 0.03 |
| Fe           | 0.52 | 0.33 | 0.38 | 0.56 | -0.07| 0.16 |
| Co           | 0.46 | 0.38 | 0.57 | 0.44 | 0.17 | 0.10 |
| Ni           | 0.37 | 0.23 | 0.58 | -0.12| 0.14 | -0.06|
| Cu           | -0.04| 0.61 | 0.30 | 0.33 | 0.17 | 0.39 |
| Zn           | 0.03 | 0.05 | 0.84 | 0.06 | 0.12 | 0.25 |
| As           | 0.26 | 0.09 | 0.19 | 0.07 | 0.86 | 0.08 |
| Mo           | -0.03| 0.30 | 0.13 | 0.06 | 0.85 | -0.18|
| Cd           | 0.08 | 0.21 | 0.68 | -0.06| 0.42 | -0.15|
| Sb           | 0.32 | 0.28 | 0.43 | 0.01 | 0.64 | 0.16 |
| Ti           | 0.13 | 0.61 | 0.43 | -0.29| 0.43 | -0.05|
| Pb           | 0.23 | -0.05| 0.20 | 0.38 | 0.29 | 0.51 |
| U            | 0.72 | 0.27 | 0.16 | 0.46 | 0.26 | 0.05 |
| EC           | 0.73 | 0.49 | 0.31 | 0.18 | 0.15 | 0.02 |
| HCO$_3^-$     | 0.92 | -0.03| -0.02| 0.07 | 0.07 | 0.05 |
| Cl$^-$       | 0.34 | 0.76 | 0.28 | -0.05| 0.19 | -0.08|
| SO$_4^{2-}$  | 0.66 | 0.43 | 0.41 | -0.09| 0.29 | 0.09 |
| Na$^+$       | 0.30 | 0.75 | 0.26 | 0.37 | 0.21 | -0.01|
| K$^+$        | 0.50 | 0.64 | 0.20 | 0.41 | 0.12 | 0.00 |
| Mg$^{2+}$    | 0.88 | 0.24 | 0.19 | 0.13 | 0.09 | 0.04 |
| Ca$^{2+}$    | 0.92 | 0.27 | 0.18 | -0.01| 0.08 | -0.01|
| NH$_4^+/-$N  | 0.24 | 0.32 | 0.50 | 0.38 | 0.26 | -0.05|
| NO$_3^-$     | 0.05 | 0.11 | 0.16 | 0.86 | 0.04 | 0.14 |

Eigenvalues: 5.59 4.16 3.84 3.07 2.83 1.30
Variance (%): 21.48 16.00 14.77 11.82 10.87 4.98
Cumulative (%): 21.48 37.48 52.25 64.07 74.94 79.93
a. Bold values represent strong loadings (>0.5).
metals and ions in the dry season had a greater impact on the Ganjiang River basin than in the wet season.

Discussion

Sources Identification

Due to the differences of geographical, environment and anthropogenic activities, the sources of heavy metals pollution in different regions have great differences [9, 11]. However, within the same watershed, the geographical environment is basically the same, and human activities are the main factors leading to the differences [4]. Multivariate statistics analysis are an effective method to identify underlying relationships between variables, and strong correlation among elements indicates their similar chemical properties and common sources [38].

In this study, we found that Fe, U, SO$_4^{2-}$, Ca$^{2+}$, Mg$^{2+}$ and HCO$_3^-$ showed a significant correlation, indicating similar sources (Fig. 5 and Table 3). The high concentration values were distributed in the zones of C2 and C3, especially in the Yuan River basin (Fig. S2). Zn, Cd, Mn, Ni, Co and NH$_4^+$ also had similar spatial variation patterns, and high concentration values were distributed in C2 (including the Zhang, Tao and Yuan River basins). Previous studies have revealed that SO$_4^{2-}$ in river water was an important indicator of anthropogenic activities, especially in mining areas [12, 39, 40]. Xinyu city is a typical industrial city with abundant coal and iron storage [41]. Research results have shown that coal mining effluent [42], coal gangue dumping [43], and coal ash released by burning would cause heavy metal pollution [44]. Coal combustion also produced large amounts of SO$_4^{2-}$, which in turn dissolved metals and non-metallic elements in minerals [12, 45]. Moreover, steel smelting wastewater dispersed into river, resulting in increased heavy metals concentrations in river water as well. The Zhang and Tao Rivers are enrichment areas for tungsten and rare earth minerals [27-29]. Hence, we inferred that the elevated level of these metals in the region can be ascribed to large amounts of wastewater produced by tungsten mining and beneficiation operations, which is in agreement with the results of other studies in the Ganjiang River basin [21, 46].

V, Cu, Ti, Na$^+$, K$^+$ and Cl$^-$ showed similar variations, and high concentration values were mainly distributed in the Shu River basin, which belongs to the Jitai Basin – the second largest commodity grain base and the largest citrus production base in Jiangxi Province. Large-scale use of chloride fertilizer and potassium fertilizer may be the main source, as reported by Samantara et al. [47]. Moreover, the application of Cu-based fungicides, pig manure and metal-contaminated biosolids were important inputs to agricultural soils [48]. As, Mo and Sb also showed high concentration values in the Zhang River basin. Southern Jiangxi Province is not only a non-ferrous metal enrichment area, but also an important agricultural field and navel orange planting area. The use of pesticides and fertilizers and the changes of land use patterns in mountainous areas leading to the release of heavy metals in rocks, which have been considered important reasons causing higher concentrations of these metals in the basin [18, 49, 50]. Arsenic is considered to be a highly toxic and carcinogenic inorganic pollutant that has attracted more and more attention around the world [51, 52]. Jia et al. [53] thought that the cause of high As in drinking water can be explained by three mechanisms, including microbial reduction and dissolution of Fe oxide minerals, desorption by competitive anions and subsequent reduction and release of As (V). In contrast, the toxicity of Sb in drinking water has not received much attention. Some studies have reported that both Sb and As are chalcophilic group V metalloids, which have similar chemistry and toxicity in the environment [54]. Meng et al. [55] proposed that Sb and As are readily dissolved from ores and rocks and released and transported into water bodies and sediments.

NO$_3^-$ was significantly positively correlated with Al and Fe (Table 3), and the higher concentration values were distributed in the Tao and Yuan Rivers. Samantara et al. [47] demonstrated that NO$_3^-$ was an important ion that reflected human activities, mainly from farmland fertilization, livestock manure, urban sewage discharge and mining activities. However, Wang et al. [41], utilizing nitrogen isotopes technology, found that the high NO$_3^-$ concentration in the Yuan River was related to industrial wastewater, while in the Tao River NO$_3^-$ was from the large amount of chemical fertilizers and agrochemicals from orange planting. In addition, the main soil type in Jiangxi Province is lateritic soil, which is known to contain large amounts of aluminum and iron. Soil erosion may also be an important pathway of Fe, Al and NO$_3^-$ flow into rivers in humid subtropical monsoon climate regions. As some studies have reported, common anthropogenic sources, including mineral exploring, smelting, engineering of steel and glass could also be an important contributor of those metals in rivers [6].

Cr showed low spatial variation, and had no significant correlation to other parameters. Undoubtedly, the source of Cr could be ascribed to lithogenic control, and as reported by other studies [56, 57]. However, in contrast to the present study, other researchers have shown that high Cr concentrations in a river are mainly the result of intensive human activities such as production of dyes, textiles and various alloys [49, 58]. The high concentration of Pb was mainly distributed in the Zhang River and Shangyou River basin, which may be related to agricultural activities. Nonetheless, other possible sources of Pb, such as leaded gasoline, domestic sewage and atmospheric deposition, cannot be excluded [58].

Taken together, our results indicate that heavy metal pollution sources of the Ganjiang River basin were...
various, and mining industries and agricultural activities were the main sources. In addition, the Yuan River basin and upstream of the Ganjiang River (in southern Jiangxi Province) were the most polluted areas.

Pollution Level and Health Risk Assessment

Low concentrations of metal, as micronutrients, are essential for life processes, but once they exceed the threshold they may pose a toxic threat to health [2, 59]. In this study, we found several elements (including Fe, Al, As, Mn and Tl) whose concentrations exceeded China’s water quality standard at some sampling sites. The comparison of those heavy metals in the Ganjiang River with other rivers in the world is shown in Table 4. According to the results, we found that concentrations of Fe and Al were relatively higher than the majority of rivers, whereas the concentrations of As and Mn were lower than in other rivers. The main reason for the differences was that the landscapes of different river basins were different, and the main sources of pollution were also different. For instance, Nakkavagu stream flowed through industrial and residential areas and received a large amount of sewage containing As and Mn elements, resulting in higher concentrations of metals in the river [60].

According to health risk assessment (Fig. 3), we found the number of sampling sites and HI values of the dry season exceeding the reference value were significantly higher than those of the wet season. The results indicated that Ganjiang River water in the dry season was more likely to pose a threat to human health. On the contrary, rich rainfall and runoff during the wet season effectively diluted the concentration of heavy metals, thereby reducing the risk of contamination [4]. Compared with adults, we found that children were more sensitive to heavy metal pollution. The result was consistent with many studies [24, 63]. Consequently, with the weak immune function and low education level of children, considerable attention should be paid to them.

Based on carcinogenic risks assessment, the result showed that As was the largest contributor to carcinogenic and non-carcinogenic effects on local residents, especially sensitive children (Fig. 4). Zhang et al. [24] also found that As was the main pollutant in the Ganjiang River. Similarly, As pollution has been found in other regions in China and other countries, such as the Chinese Loess Plateau [2], Three Gorges Reservoir [11] and 14 countries in Latin America [51]. Numerous studies have confirmed that excessive intake of arsenic can cause various carcinogenic risks and such unhealthy effects as liver cancer, bladder cancer, skin cancer, hypertension, neuropathy, and vascular diseases [2, 52]. Overall, all these findings suggest that health risks caused by As should be paid attention to.

However, since this study only analyzed the dissolved heavy metals in water, it did not analyze sediments, suspended solid metals and different fractions of heavy metals in water. Previous studies have demonstrated that the concentration of heavy metals in sediments is three to five times higher than those in the surface water [59]. Due to seasonal hydrological changes, such as hydrodynamic disturbances, redox potentials, water temperatures and pH values, different fractions of heavy metals could be absorbed and desorbed as well, resulting in secondary pollution [8, 56]. In addition, there existed some uncertainties of the risk assessment parameters, including ED (exposure duration), BW (body weight), SA (exposed skin area) and so on, depending on different regions, different pollution sources and receptors [37, 39]. Hence, more work should be carried out in the basin in order to protect aquatic ecosystems.

Conclusions

Heavy metal pollution has drawn worldwide attention in recent decades. Similarly, heavy metal pollution in China is one of the hottest topics. The aim of this study was to look at the characteristics and sources of heavy metals and their potential risk assessment...
in the Ganjiang River basin. Results showed that the concentrations of hydrochemical ions and heavy metals exhibited significant seasonal variations and spatial heterogeneity. Several metals selected in this study (including Fe, Al, As, Mn and Ti) had concentrations that exceeded the water quality standard at some sampling sites. Mining industries and agricultural activities were the main sources of heavy metal pollution in the Ganjiang River basin, while the Yuan River basin and upstream of Ganjiang River (the southern of Jiangxi Province) were the most polluted areas. Based on health risk assessment, ingestion was the main pathway that posed an adverse challenge and risk to human health, and As was the largest contributor, causing carcinogenic and non-carcinogenic risks to humans – in particular for children, who should be paid more attention from local governments to control and manage the pollution.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (41661017, 41201033), the Natural Science Foundation of Jiangxi Province, and the Collaborative Innovation Center for Major Ecological Security Issues of Jiangxi Province and Monitoring Implementation [JXS-EW-00]. We acknowledge the editors and reviewers for polishing the language of our paper and for their in-depth discussion.

Conflict of Interest

The authors declare no conflict of interest.

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Fig. S1. Spatial-temporal variabilities of physico-chemistry parameters in 37 sampling sites from Ganjiang River basin.
Fig. S2. Spatial-temporal variabilities of 16 heavy metals in 37 sampling sites from Ganjiang River basin.
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Fig. S3. Dendrogram based on hierarchical clustering analysis for the 37 sampling sites in the Ganjiang River basin.

Fig. S4. Sampling sites based on hierarchical clustering analysis in the Ganjiang River basin.
Fig. S5. Principal component analysis (PCA) of heavy metals and hydrochemical ions in Ganjiang River basin (individuals: 1~37 stand for the sampling site G1~G37 in the dry season and 38~74 stand for sampling sites G1~G37 in the wet season; cos2 values are used to estimate the quality of the representation).
Table S1. Dermal permeability coefficient, reference dose and hazard quotient for heavy metals in Ganjiang River basin.

| Element | Deason | Kp (cm/h) | RDingestion (ug/kg/day) | RIdermal (ug/kg/day) | HQingestion Adult | Child | HQdermal Adult | Child | HI |
|---------|--------|-----------|-------------------------|----------------------|-------------------|-------|----------------|-------|-----|
| Be      | dry    | 1.00E-03  | 2                       | 1                    | 3.30E-06          | 1.05E-05 | 4.63E-06       | 7.92E-06 | 7.92E-06 |
| Be      | wet    | 1.00E-03  | 2                       | 1                    | 8.12E-07          | 2.59E-06 | 1.14E-06       | 1.95E-06 | 1.95E-06 |
| Al      | dry    | 1.00E-03  | 1000                    | 200                  | 5.63E-03          | 1.79E-02 | 1.38E-04       | 2.37E-04 | 5.77E-03 |
| Al      | wet    | 1.00E-03  | 1000                    | 200                  | 3.46E-04          | 1.10E-03 | 8.50E-06       | 1.45E-05 | 3.55E-04 |
| V       | dry    | 1.00E-03  | 5                       | 0.13                 | 1.93E-04          | 6.14E-04 | 1.40E-03       | 2.40E-03 | 1.59E-03 |
| V       | wet    | 1.00E-03  | 5                       | 0.13                 | 1.27E-04          | 4.06E-04 | 9.26E-06       | 1.58E-03 | 1.05E-03 |
| Cr      | dry    | 2.00E-03  | 3                       | 0.075                | 1.18E-03          | 3.75E-03 | 1.85E-02       | 3.17E-02 | 1.97E-02 |
| Cr      | wet    | 2.00E-03  | 3                       | 0.075                | 1.20E-03          | 3.82E-03 | 1.89E-02       | 3.23E-02 | 2.01E-02 |
| Mn      | dry    | 1.00E-03  | 24                      | 0.96                 | 3.98E-02          | 1.27E-01 | 4.89E-03       | 8.36E-03 | 4.47E-02 |
| Mn      | wet    | 1.00E-03  | 24                      | 0.96                 | 2.16E-02          | 6.86E-02 | 2.65E-03       | 4.53E-03 | 2.42E-02 |
| Fe      | dry    | 1.00E-03  | 700                     | 140                  | 1.45E-02          | 4.60E-02 | 3.55E-04       | 6.08E-04 | 1.48E-02 |
| Fe      | wet    | 1.00E-03  | 700                     | 140                  | 4.57E-03          | 1.45E-02 | 1.12E-04       | 1.92E-04 | 4.68E-03 |
| Co      | dry    | 4.00E-04  | 0.3                     | 0.06                 | 2.35E-02          | 7.47E-02 | 2.30E-04       | 3.94E-04 | 2.37E-02 |
| Co      | wet    | 4.00E-04  | 0.3                     | 0.06                 | 8.44E-03          | 2.68E-02 | 8.28E-05       | 1.42E-04 | 8.52E-03 |
| Ni      | dry    | 2.00E-04  | 20                      | 0.8                  | 1.32E-04          | 4.21E-04 | 8.12E-05       | 1.39E-04 | 2.14E-04 |
| Ni      | wet    | 2.00E-04  | 20                      | 0.8                  | 8.22E-05          | 2.62E-04 | 5.04E-05       | 8.63E-05 | 1.33E-04 |
| Cu      | dry    | 1.00E-03  | 40                      | 8                    | 1.77E-03          | 5.63E-03 | 7.61E-05       | 1.30E-04 | 1.84E-03 |
| Cu      | wet    | 1.00E-03  | 40                      | 8                    | 8.53E-04          | 2.71E-03 | 3.67E-05       | 6.28E-05 | 8.90E-04 |
| Zn      | dry    | 6.00E-04  | 300                     | 60                   | 1.63E-04          | 5.19E-04 | 1.20E-05       | 2.06E-05 | 1.75E-04 |
| Zn      | wet    | 6.00E-04  | 300                     | 60                   | 1.43E-04          | 4.54E-04 | 1.05E-05       | 1.80E-05 | 1.53E-04 |
| As      | dry    | 1.00E-03  | 0.3                     | 0.285                | 7.86E-01          | 2.50E+00 | 4.28E-03       | 7.32E-03 | 7.91E-01 |
| As      | wet    | 1.00E-03  | 0.3                     | 0.285                | 2.85E-01          | 9.07E-01 | 1.55E-03       | 2.65E-03 | 2.87E-01 |
| Mo      | dry    | 1.00E-03  | 5                       | 1.9                  | 2.24E-02          | 7.13E-02 | 2.89E-04       | 4.95E-04 | 2.27E-02 |
| Mo      | wet    | 1.00E-03  | 5                       | 1.9                  | 1.19E-02          | 3.78E-02 | 1.53E-04       | 2.62E-04 | 1.20E-02 |
| Cd      | dry    | 1.00E-03  | 0.5                     | 0.025                | 8.49E-04          | 2.70E-03 | 1.67E-03       | 2.85E-03 | 2.52E-03 |
| Cd      | wet    | 1.00E-03  | 0.5                     | 0.025                | 4.06E-04          | 1.29E-03 | 7.96E-04       | 1.36E-03 | 1.20E-03 |
| Sb      | dry    | 1.00E-03  | 0.4                     | 0.06                 | 3.14E-03          | 9.98E-03 | 6.84E-04       | 1.17E-03 | 3.82E-03 |
| Sb      | wet    | 1.00E-03  | 0.4                     | 0.06                 | 3.14E-03          | 9.98E-03 | 6.84E-04       | 1.17E-03 | 3.82E-03 |
| Tl      | dry    | 1.00E-03  | 0.01                    | 0.01                 | 1.42E-01          | 4.51E-01 | 6.96E-04       | 1.19E-03 | 1.42E-01 |
| Tl      | wet    | 1.00E-03  | 0.01                    | 0.01                 | 1.28E-01          | 4.07E-01 | 6.28E-04       | 1.07E-03 | 1.28E-01 |
| Pb      | dry    | 1.00E-04  | 1.4                     | 0.42                 | 6.37E-03          | 2.03E-02 | 3.48E-05       | 5.95E-05 | 6.41E-03 |
| Pb      | wet    | 1.00E-04  | 1.4                     | 0.42                 | 4.35E-03          | 1.38E-02 | 2.37E-05       | 4.06E-05 | 4.38E-03 |
| U       | dry    | 1.00E-03  | -                       | -                    | -                 | -      | -              | -      | -    |
| U       | wet    | 1.00E-03  | -                       | -                    | -                 | -      | -              | -      | -    |
Table S2. Carcinogenic risk results of Cr, As and Pb in Ganjiang River basin.

| Element | Season | \( \text{ABS}_{\text{cal}} \) | CSF ingestion | CSF dermal | CR ingestion | CR dermal | CR total |
|---------|--------|-----------------|---------------|-------------|---------------|------------|----------|
|         |        |                 | Adult | Child | Adult | Child | Adult | Child |
| Cr      | dry    | 0.025       | 5.00E-01   | 2.00E+01 | 1.77E-06 | 5.63E-06 | 2.78E-05 | 4.75E-05 | 2.95E-05 | 5.32E-05 |
| Cr      | wet    | 0.025       | 5.00E-01   | 2.00E+01 | 1.80E-06 | 5.73E-06 | 2.83E-05 | 4.84E-05 | 3.01E-05 | 5.41E-05 |
| As      | dry    | 0.95        | 1.50E+00   | 1.58E+00 | 3.54E-04 | 1.13E-03 | 1.92E-06 | 3.29E-06 | 3.56E-04 | 1.13E-03 |
| As      | wet    | 0.95        | 1.50E+00   | 1.58E+00 | 1.28E-04 | 4.08E-04 | 6.98E-07 | 1.19E-06 | 1.29E-04 | 4.09E-04 |
| Pb      | dry    | 0.3         | 8.50E-03   | 2.83E-02 | 7.58E-08 | 2.41E-07 | 4.14E-10 | 7.08E-10 | 7.63E-08 | 2.42E-07 |
| Pb      | wet    | 0.3         | 8.50E-03   | 2.83E-02 | 5.18E-08 | 1.65E-07 | 2.83E-10 | 4.83E-10 | 5.21E-08 | 1.65E-07 |