

Distribution, source, water quality and health risk assessment of dissolved heavy metals in major rivers in Wuhan, China

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ABSTRACT

Heavy metals are released into the water system through various natural processes and anthropogenic activities, thus indirectly or directly endangering human health. The distribution, source, water quality and health risk assessment of dissolved heavy metals (V, Mn, Fe, Co, Ni, Zn, As, Mo, Sb) in major rivers in Wuhan were analyzed by correlation analysis (CA), principal component analysis (PCA), heavy metal pollution index (HPI), hazard index (HI) and carcinogenic risk (CR). The results showed that the spatial variability of heavy metal contents was pronounced. PCA and CA results indicated that natural sources controlled Mn, Fe, Co, Ni and Mo, and industrial emissions were the dominant factor for V, Zn and Sb, while As was mainly from the mixed input of urban and agricultural activities. According to the heavy metal pollution index (HPI, ranging from 23.74 to 184.0) analysis, it should be noted that As and Sb contribute most of the HPI values. The health risk assessment using HI and CR showed that V and Sb might have a potential non-carcinogenic risk and As might have a potential carcinogenic risk to adults and children in the study area (CR value exceeded target risk 10^{-4}). At the same time, it was worth noting that As might have a potential non-carcinogenic risk for children around QLR (HI value exceeded the threshold value 1). The secular variation of As and Sb should be monitor in high-risk areas. The results of this study can provide important data for improving water resources management efficiency and heavy metal pollution prevention in Wuhan.

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INTRODUCTION

With the rapid development of the social economy, industry, agriculture, medicine, and mining activities are increasing, which have seriously affected the quality of surface water worldwide (*Gao et al., 2020; Wang et al., 2017; Zeng, Han & Yang, 2020*). Heavy metals have the characteristics of toxicity, persistence and bioaccumulation, which cause

environmental pollution to the water ecosystem and threaten human health (Cameron, Mata & Riquelme, 2018; Zaric et al., 2018; Zeng et al., 2019). There are two main exposure pathways (direct ingestion and dermal absorption) of heavy metals in water bodies (Gao et al., 2020; Giri & Singh, 2014). However, aquatic foods and plants as human food sources may also lead to the exposure of heavy metals in water (Krishnamurti et al., 2015; Qu et al., 2018). Therefore, due to the bioaccumulation of heavy metals, even if humans do not directly drink or contact water contaminated by heavy metals, they will also be exposed to high levels of heavy metals from food (Antoniadis et al., 2016; Jiang et al., 2016). Thus, the pollution of heavy metals in the water environment has been widely concerned worldwide (Ali et al., 2016; Chowdhury et al., 2016; Zeng & Han, 2020a; Zeng & Han, 2020b).

Heavy metals enter the water body mainly through natural processes (atmospheric dry/wet deposition, rock weathering and volcanism) and anthropogenic activities (industrial, agricultural, medical and urban sewage) (Han & Liu, 2004; Han et al., 2019; Krishna, Satyanarayanan & Govil, 2009; Li & Zhang, 2010; Meng et al., 2016). The metal availability of organisms is determined by the concentration and species of heavy metals in water. Therefore, more attention should be paid to heavy metals in surface water because these heavy metals may affect human health through food, water and body contact (Qu et al., 2018). The study of the concentration, distribution, source, water quality and health risk levels of dissolved heavy metals in surface water is the basis for the effective control of water pollution and the maintenance of water ecosystem health (Xiao, Jin & Wang, 2014; Xiao et al., 2019).

Correlation analysis (CA) and principal component analysis (PCA) are common tools for studying heavy metals in water environment. They can better identify the natural or anthropogenic sources of heavy metals (Gao et al., 2020; Giri & Singh, 2014; Qu et al., 2018; Thuong et al., 2013; Wang et al., 2017; Xiao et al., 2019). Furthermore, heavy metal pollution index (HPI) was used to analyze the combined effects on water quality (Tiwari et al., 2015). Hazard quotient (HQ), hazard index (HI) and carcinogenic risk (CR) are commonly used to assess human health risks of heavy metals (Qu et al., 2018; Wang et al., 2017; Wu et al., 2009b; Zeng et al., 2019). Moreover, geographical information system (GIS) is also used to show the spatial distribution of pollutants (Qu et al., 2018; Tiwari et al., 2015).

With the growth of population and the rapid development of agriculture, cities and industries in the past decades, rivers in Wuhan have been polluted by toxic heavy metals (Gong et al., 2018; Xu et al., 2020a). Therefore, the sources and health risks associated with heavy metals in these rivers need to be explored to protect water resources and improve water quality. Heavy metal pollution in surface water and sediment in Wuhan has been studied a lot (Du et al., 2014; Hu et al., 2012; Yang et al., 2016). However, the systematic study on geochemical characteristics, sources, water quality and health risks of dissolved heavy metals in surface rivers of Wuhan is still lacking, especially in the analysis of spatial distribution and potential health hazards of heavy metals in surface rivers through different exposure pathways and source identification.

In this study, water from surface rivers in Wuhan was collected systematically. Nine dissolved heavy metals in the river water were analyzed, with the following objectives: (1) to understand the spatial distribution of heavy metals in surface rivers; (2) to explore the potential sources of heavy metals; (3) to evaluate river water quality and the risk level of heavy metals to human health, and to map their spatial distribution. The results can provide important information for water resources management and prevention and control of heavy metal pollution to reduce the health hazards to the public.

MATERIALS AND METHODS

Study area

Wuhan is located in the central part of China and the middle reaches of the Yangtze River basin (29°58′-31°22′N; 113°41′-115°05′E), which is the capital of Hubei Province and the central city of Yangtze River Economic Zone. The landform belongs to the transition region from the southeast hills of Hubei through the eastern margin of Jiangnan Plain to the lower elevations at the southern foot of the Dabie Mountains. The climate of Wuhan belongs to the north subtropical monsoon climate, with a mean annual temperature of between 15.8 °C and 18.5 °C. The annual precipitation ranges from 1,150 to 1,450 mm, of which about 40% occurs in the rainy season (June to July). With a developed water system and rivers, Wuhan has formed a complex and unique water area with a total water area of 2,217.6 km² (Xu & Wang, 2020). Eight representative rivers are selected in this study, which are Yangtze River (YR), Dongjing River (DJR), Han River (HR), Qingling River (QLR), Xunsi River (XSR), Fu River (FR), Sheshui River (SSR) and Daoshui River (DSR) (Fig. 1). The lithology of the basin is mainly carbonate rock (Guan, Meng & Zhou, 2008). Wuhan industry is developed, including automobile, chemical, steel, metallurgy, etc. Heavy metal pollution in rivers is becoming more and more severe due to the long-term acceptance of untreated domestic and industrial wastewater (Li, 2019).

Sample collection and analysis

In July 2019, 34 surface water samples were collected from eight rivers in Wuhan, of which YR1~9 HR1~5, DJR1~3, FR1~9, XSR1~2, QLR1~2, DSR1~2, SSR1~2 (Fig. 1), which reasonably reflected the water quality of surface rivers in Wuhan. After collection, the samples were immediately filtered with 0.22 µm acetate fiber filter membrane and acidified with ultra-pure concentrated HNO₃ to pH < 2, then sealed in a pre-pickled polyethylene bottle and stored in a 4 °C freezer for the determination of heavy metals. The remaining unfiltered water samples were acidified with sulfuric acid to pH < 2 to determine total phosphorus and total nitrogen. The pH, electrical conductivity (EC) and dissolved oxygen (DO) were measured by portable water quality analyzer (WTW Company, Weilheim, Upper Bavaria, Germany). Nine heavy metal elements (V, Mn, Fe, Co, Ni, Zn, As, Mo and Sb) in water samples were determined by inductively coupled plasma-mass spectrometry (ICP-MS, NexION300X) of the Institute of Geochemistry, Chinese Academy of Sciences. Standard reference materials (GSB04-1767-2004) were used for method validation and quality control (Liu & Han, 2021; Xu et al., 2020a; Zhang et al., 2018). All samples, standards and program blanks of the same batch of samples were

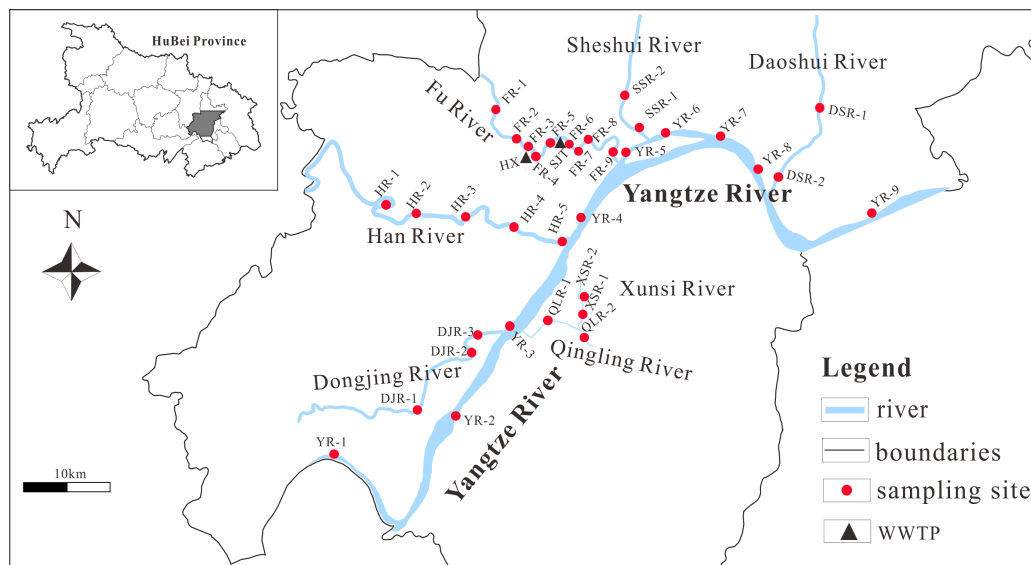


Figure 1 Sample sites distribution of the studied rivers in Wuhan.

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analyzed. The recoveries ranged from 90.0% to 110.4%. The relative standard deviation of heavy metals is $\pm 5\%$.

Statistical analysis

In this study, correlation analysis (CA) and principal component analysis (PCA) were used to identify pollution sources. PCA is a common statistical analysis method in studying the sources of heavy metal pollution (Loska & Wiechuła, 2003; Zeng, Han & Yang, 2020). In the PCA analysis of the data, the feasibility of the data was tested by Kaiser–Meyer–Olkin (KMO) and Bartlett’s sphericity test ($p < 0.001$) (Varol, 2011). The principal components were extracted only when the eigenvalue is greater than or equal to 1 (Kowalkowski et al., 2006). All data were processed by SPSS 22.0.

Heavy metal pollution index

Heavy metal pollution index (HPI) can provide the comprehensive impact of a single heavy metal on the overall water quality. The HPI model (Mohan, Nithila & Reddy, 2008; Qu et al., 2018) is given by Eq. (1)

$$\text{HPI} = \frac{\sum_{i=1}^n (Q_i W_i)}{\sum_{i=1}^n W_i} \quad (1)$$

$$Q_i = \frac{C_i}{S_i} \times 100 \quad (2)$$

$$W_i = \frac{k}{S_i} \quad (3)$$

where W_i is the unit weight of the i th parameter, which can reflect its importance. Q_i is the sub-index of the i th heavy metal parameter, and n is the number of parameters selected in

the study. c_i is the concentration of the i th heavy metal parameter ($\mu\text{g/L}$), and s_i is the highest allowable value of the i th parameter in drinking water standard. The value of s_i in this study is from the World Health Organization (WHO) drinking water quality guidelines (WHO, 2011). Where k is the proportional constant, here we take K as “1”, which is convenient for calculation (Wanda, Gulula & Phiri, 2012). Now we typically use the modified scale to describe heavy metal pollution: low (HPI values < 15), medium (HPI values within 15–30) and high (HPI values > 30) (Tiwari et al., 2015).

Geographic information system (GIS) is widely used to collect various spatial data to express spatial variation (Gupta & Srivastava, 2010; Qu et al., 2018; Tiwari et al., 2015). Therefore, GIS technology was used to present the results of the HPI assessment of river heavy metal ecological risk in Wuhan. The HPI values of the sampling points were inserted into the surface rivers of Wuhan by inverse distance weighted (IDW) method to show the spatial distribution. A spatial distribution map was compiled by ArcGIS 10.7 software.

Human health risk assessment model

Heavy metals are difficult to remove in water, and they can be recycled and bioaccumulated through a biochemical reaction process. Therefore, people need to pay attention to their harmful effects on human health and environmental impact on aquatic ecosystem (Waalkes, 2000; Wang et al., 2017; Wu et al., 2009a). Therefore, to facilitate the determination of appropriate management measures, the toxicity of heavy metals in the water system is worth studying (Lemly, 1996). In this study, hazard quotient (HQ) and hazard index (HI) were used to assess the health risk of heavy metals in rivers of Wuhan (Meng et al., 2016). Heavy metals in the water environment enter human body mainly through direct ingestion and dermal absorption (Giri & Singh, 2014; Zeng et al., 2019). HQ is estimated by the ratio of exposure to reference dose (RfD) in various pathways. HI is the sum of the HQs of the two main exposure pathways mentioned above, which can be used to represent the total potential non-carcinogenic risk of individual heavy metals. When HQ/HI is greater than 1, the pollution level may cause harm to human health, and there is a non-carcinogenic risk, which needs particular attention; however, when HQ/HI is less than 1, there is no health risk (Tripathee et al., 2016; Yi, Yang & Zhang, 2011). The calculation formula of HQ and HI is as follows:

$$\text{ADD}_{\text{ingestion}} = (C_w \times \text{IR} \times \text{EF} \times \text{ED}) / (\text{BW} \times \text{AT}) \quad (4)$$

$$\text{ADD}_{\text{dermal}} = (C_w \times \text{SA} \times K_p \times \text{ET} \times \text{EF} \times \text{ED} \times 10^{-3}) / (\text{BW} \times \text{AT}) \quad (5)$$

$$\text{HQ} = \text{ADD} / \text{RfD} \quad (6)$$

$$\text{RfD}_{\text{dermal}} = \text{RfD} \times \text{ABS}_{\text{GI}} \quad (7)$$

$$\text{HI} = \sum \text{HQs} \quad (8)$$

where $\text{ADD}_{\text{ingestion}}$ is the average daily doses of direct intake ($\mu\text{g/kg/day}$); $\text{ADD}_{\text{dermal}}$ is the average daily doses of skin absorption ($\mu\text{g/kg/day}$); C_w is the concentration of heavy

metals in each water sample ($\mu\text{g/L}$); IR is the ingestion rate (L/ day); EF is the exposure frequency (days/year); ED is the exposure duration (years); AT is the average time (days); BW is the average body weight for adults and children (kg); ET is the daily exposure time (h/day); SA is the area of skin exposure (cm^2); K_p is the dermal permeability coefficient in water (cm/h); RfD is the corresponding reference dose ($\mu\text{g/kg/day}$); ABS_{GI} is the gastrointestinal absorption factor (dimensionless). The values of these parameters come from (*United States Environmental Protection Agency, 2009; Wang et al., 2017; Wu et al., 2009b*).

The carcinogenic risk of heavy metals is evaluated by Eq. (9). Carcinogenic risk represents the increased probability of cancer due to chemical exposure (*Chen & Liao, 2006; Obiri et al., 2006*). CR values in US-EPA are divided into three levels: (1) CR value less than 10^{-6} indicates negligible level; (2) $10^{-6} < \text{CR} < 10^{-4}$ is acceptable level; (3) $\text{CR} > 10^{-4}$ indicates high cancer risk to human (*Qu et al., 2018*).

$$\begin{cases} \text{CR} = \text{ADD} \times \text{SF}, & \text{ADD} \times \text{SF} < 0.01 \\ \text{CR} = 1 - \text{EXP}(-\text{ADD} \times \text{SF}), & \text{ADD} \times \text{SF} \geq 0.01 \end{cases} \quad (9)$$

In this study, carcinogenic and non-carcinogenic risk assessments were performed for As, which was carcinogenic to humans. For the other eight heavy metals (V, Mn, Fe, Co, Ni, Zn, Mo, Sb), only non-carcinogenic risk assessments were considered. The HI and CR values of the sampling points were interpolated into the surface rivers of Wuhan by the IDW method to show the spatial distribution of non-carcinogenic risk and carcinogenic risk.

RESULTS

Kolmogorov–Smirnov test of data

The normal distribution of the data in this study was tested by Kolmogorov–Smirnov (K–S) statistics (*Table 1*). Results indicated that only vanadium and dissolved oxygen were normal distribution. It could be seen from the test results that the average concentration of heavy metals might be seriously affected by the abnormal values of water samples. Therefore, the median concentrations were used for calculation. However, arithmetic means were used for comparison because the values in the drinking water standards are generally given as arithmetic means.

Physicochemical characteristics

The water quality parameters (pH, EC, DO) of water samples are exhibited in *Table 1*. The pH value of the river water ranged from 5.51 to 9.14, with a mean of 7.96, demonstrating slight alkalinity characteristics. The DO ranged from 2.59 to 19.24 mg/L, with a mean of 7.75 mg/L. The EC ranged from 213.0 to 661.0 $\mu\text{S/cm}$, with a mean of 344.0 $\mu\text{S/cm}$. In a word, pH, EC and DO had pronounced variability in rivers in Wuhan.

Table 1 Concentrations of dissolved heavy metals ($\mu\text{g/L}$), pH, EC ($\mu\text{s/cm}$) and DO (mg/L) in rivers in Wuhan.

	Min	Max	Mean	Median	SD	K-S test ^a
V	0.54	3.20	1.91	1.85	0.64	0.200
Mn	0.00	7.66	0.90	0.16	1.88	0.000
Fe	8.62	21.97	12.80	12.18	2.77	0.008
Co	0.03	0.19	0.06	0.05	0.04	0.000
Ni	0.46	3.77	1.16	0.86	0.72	0.000
Zn	0.39	7.45	2.10	1.52	1.81	0.000
As	2.51	11.15	3.72	3.13	1.74	0.000
Mo	1.07	6.00	2.28	1.73	1.26	0.000
Sb	1.14	16.29	4.29	4.07	2.73	0.100
pH	5.51	9.14	7.96	7.95	0.75	0.011
EC	213.00	661.00	344.00	329.03	92.71	0.013
DO	2.59	19.24	7.75	6.82	3.26	0.540

Note:

^a Kolmogorov–Smirnov test.

Concentrations of heavy metals in river water

The concentrations of dissolved heavy metals in rivers in Wuhan are demonstrated in [Table 1](#). V, Fe, Ni, Zn, As, Mo and Sb had relatively high concentration, with mean concentrations of 1.91 $\mu\text{g/L}$, 12.80 $\mu\text{g/L}$, 1.16 $\mu\text{g/L}$, 2.10 $\mu\text{g/L}$, 3.72 $\mu\text{g/L}$, 2.28 $\mu\text{g/L}$, 4.29 $\mu\text{g/L}$, respectively. Moreover, there were a few elements whose concentration was less than 1 $\mu\text{g/L}$, represented by Mn (0.90 $\mu\text{g/L}$) and Co (0.06 $\mu\text{g/L}$). Fe, Sb and As were the most abundant metals in sampling periods.

Concentrations of dissolved heavy metals were compared with the limits for drinking water and surface water established by [China EPA \(2002, 2006\)](#), [WHO \(2011\)](#) and [Environmental Protection Administration of China \(2003\)](#) ([Table 2](#)). The total concentration (average) of all heavy metals in river water was within the three drinking water standard limits (except V, there is no corresponding standard). The concentrations of Zn and As belonged to Grade I of surface water standard, which indicated that the overall water quality of the Wuhan river water was excellent. However, Sb concentrations in YR and HR exceeded the limit values of the three drinking water standards and in FR was close to the limit. In addition, the As concentrations in DJR and QLR were significantly higher than those in other rivers, which were close to the standard limits of drinking water. These heavy metals exceeded or closed to guideline values could be considered as pollutants, which might be caused by relatively high anthropogenic input at the corresponding sampling points. For example, Sb concentration in HR and As concentration in QLR were higher than the drinking water guideline, which indicated that the two rivers were significantly affected by anthropogenic input.

[Table S1](#) shows the comparison of some heavy metals in rivers in Wuhan with other rivers in the world. Except for Mn, Fe, and Co, the average concentrations of heavy metals were higher than the world average. The average heavy metals in rivers in Wuhan were

Table 2 Comparison of heavy metal concentrations ($\mu\text{g/L}$) in rivers in Wuhan with water quality standards for drinking water and surface water.

	V	Mn	Fe	Co	Ni	Zn	As	Mo	Sb
Total	1.91	0.90	12.80	0.06	1.16	2.10	3.72	2.28	4.29
Yangtze River	1.83	0.29	11.66	0.03	0.81	1.93	3.05	1.44	5.15
Dongjin River	1.21	0.21	13.67	0.06	0.72	0.97	6.54	1.75	1.55
Qingling River	1.98	1.27	11.33	0.07	1.76	0.69	7.80	4.54	2.40
Xunsi River	1.88	3.59	17.97	0.17	2.13	1.68	4.05	4.58	2.62
Han River	2.93	1.78	14.70	0.04	0.89	4.32	3.02	3.62	6.84
Fu River	1.95	0.96	13.06	0.07	1.52	2.00	3.27	2.00	4.51
Sheshui River	1.28	0.04	10.51	0.06	0.83	1.33	2.89	1.26	3.41
Daoshui River	1.07	0.09	9.35	0.06	1.22	2.14	2.80	1.28	1.58
World average ^a	0.71	34.00	66.00	0.15	0.80	0.60	0.62	0.42	0.07
China ^b		100	300	1000	20	1000	10	70	5
WHO ^c		500	300		20	3000	10	70	5
US EPA ^d		500	300			5000	10		6
Grade ^e	I					50	50		
	II					1000	50		
	III					1000	50		
	IV					2000	100		
	V					2000	100		

Notes:^a Gaillardet, Viers & Dupré (2014).^b Chinese drinking water standards (GB 5749-2006).^c WHO (2011) drinking water guidelines.^d Environmental Protection Administration of China (2003) drinking water standards.^e Chinese surface water standards (GB 3838-2002).

lower than other rivers in China, such as Xiangjiang (Zeng *et al.*, 2015), Dan River (Meng *et al.*, 2016), Tarim River (Xiao, Jin & Wang, 2014), Zhujiang River (Zeng *et al.*, 2019), and Huai River (Wang *et al.*, 2017). The heavy metals concentrations in some developing countries were generally higher than in this study, such as Vietnam, Iran, Nigeria, India and Turkey (Eneji, Sha'Ato & Annune, 2012; Giri & Singh, 2014; Nasrabadi, 2015; Thuong *et al.*, 2013; Varol & Şen, 2012). However, in this study, the average heavy metals were higher than in some developed countries, such as the USA, France, Australia, Canada (Elbaz-Poulichet *et al.*, 2006; Gaillardet, Viers & Dupré, 2014; Markich & Brown, 1998; Warnken & Santschi, 2009). This showed that the pollution level of heavy metals in rivers in Wuhan was at a medium level.

Spatial distribution of heavy metals

Spatial distribution of heavy metals in the main stream

The spatial distribution of heavy metals in the main stream is presented in Fig. 2. In general, Fe, Mn and Co concentrations presented a slowly increasing trend from upstream to downstream. In contrast, V, Ni, Mo, Zn, As, Sb increased slowly from upstream to downstream and then decreased gradually at YR-7. It should be noted that V, Ni, Zn, As and Sb concentrations were higher at YR-7, and Mn, Fe and Mo concentrations

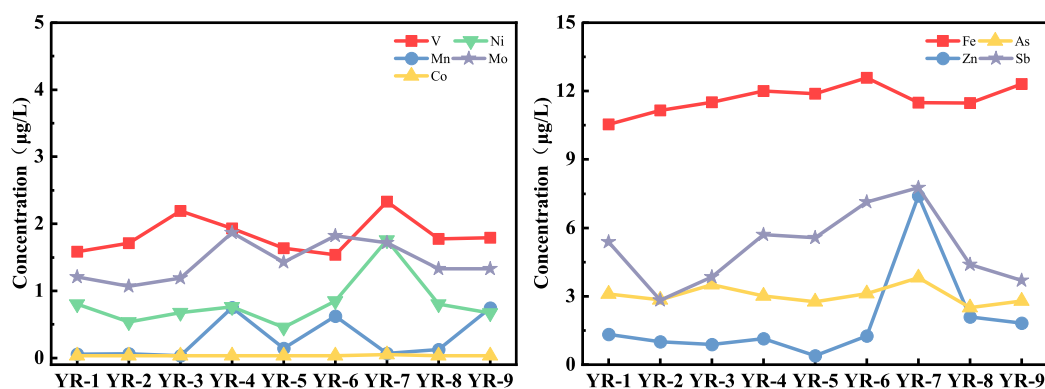


Figure 2 Spatial variations of nine heavy metals in nine sampling sites along the mainstream from Yangtze River in Wuhan. Full-size [DOI: 10.7717/peerj.11853/fig-2](https://doi.org/10.7717/peerj.11853/fig-2)

were higher at YR-4 and YR-6, while the fluctuation of Co along the main stream was not apparent. Different distribution of nine heavy metals might be affected by various local human activities, like industrial, agricultural, domestic, *etc.*

Spatial distribution of heavy metals in tributaries

The spatial distribution of each heavy metal in tributaries is exhibited in Fig. 3. The concentrations of heavy metals in QLR, XSR, HR and FR were relatively high, while those in DJR, SSR and DSR were relatively low. Although the spatial distribution showed wide variation, according to the spatial distribution characteristics of heavy metals, we could conclude three main distribution patterns: (1) the V, Zn and Sb concentrations in HR were higher than those in other rivers; (2) the Co, Fe, Mn, Ni and Mo concentrations in XSR were higher; (3) The concentration of As in QLR and DJR was higher. In addition, it was noteworthy that all heavy metals at FR-3 showed a solid upward trend, which might be related to the effluent of the Hanxi wastewater treatment plants upstream of the sampling point.

Statistical analysis

Correlation matrix can show the correlation between survey variables by presenting the overall consistency of the data set (Chen *et al.*, 2007; Helena, 2000; Wang *et al.*, 2017). In this study, to identify the likely sources of heavy metals in the rivers of Wuhan, Spearman's correlation analysis method was used to initially determine the degree of correlation between nine dissolved heavy metals. The results are shown in Fig. 4. Mn, Fe, Co, Ni and Mo were positively correlated, and the correlation coefficients ranged from 0.15 to 0.73. A significant positive correlation was observed between V and Sb ($p < 0.01$). In addition, Mo was also significantly positively correlated with V (0.47) and As (0.37).

The application of PCA can more accurately identify the sources of these heavy metals (Dong *et al.*, 2015; Kumar *et al.*, 2017). According to the Kaiser–Meyer–Olkin (KMO) value (0.73) and Bartlett's sphericity test (zero) results, the data in this study could be analyzed by PCA (Varol, 2011). Three principal components (PC) with eigenvalues > 1 (eigenvalue of 3.74 for PC1; 2.11 for PC2; and 1.19 for PC3) were extracted, explaining approximately 78.27% of the total variance. Three PCs were presented in Table 3 and

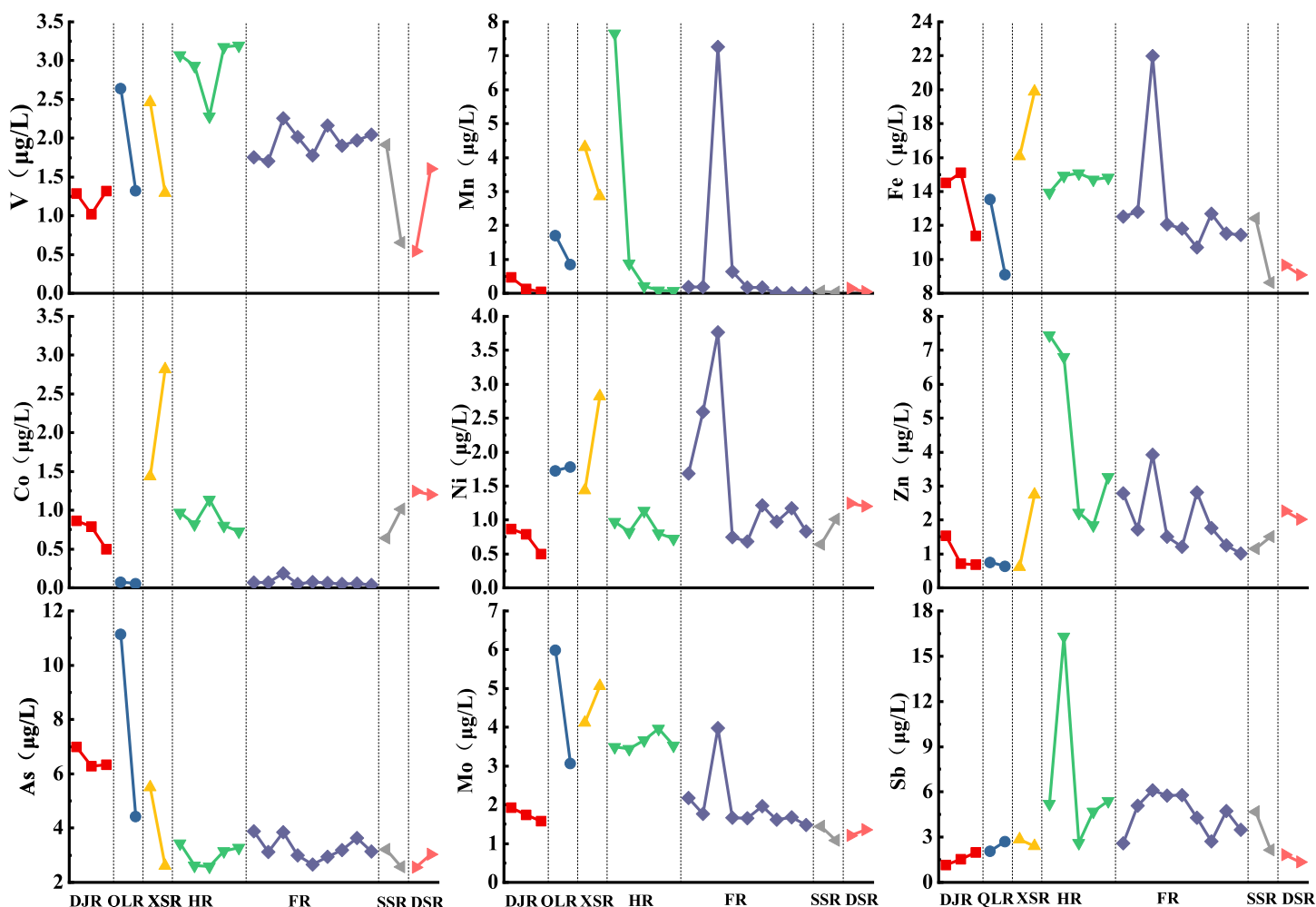


Figure 3 Spatial distribution of heavy metals in tributaries from Yangtze River in Wuhan.

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Fig. 5. In PC1, the load of Mn (0.76), Fe (0.75), Co (0.92), Ni (0.88) and Mo (0.58) was higher, which explained the variance of 35.25%. The PC2 explained 25.81% of the total variance, mainly including V (0.80), Zn (0.78) and Sb (0.84). Finally, As (0.84) and Mo (0.66) had a high load in PC3, accounting for 17.21% of the total variance.

DISCUSSION

Controlling factors for dissolved heavy metals

The content of dissolved heavy metals in water is controlled by many factors, such as pH, EC and lithology (Gao *et al.*, 2020; Xu *et al.*, 2020b). The competition of relative binding sites between metal and hydrogen ions is affected by pH (Papafilippaki, Kotti & Stavroulakis, 2008). The lower the pH value, the more intense the competition. Moreover, the lower pH may dissolve metal complexes in sediments, thereby releasing free metal ions (Gao *et al.*, 2020). However, in this study, pH was only significantly positively correlated with Co (0.365) ($p < 0.05$), but was no correlation with V, Mn, Fe, Ni, Zn, As, Mo and Sb (Fig. 4). Therefore, PH is not the primary control factor of dissolved heavy

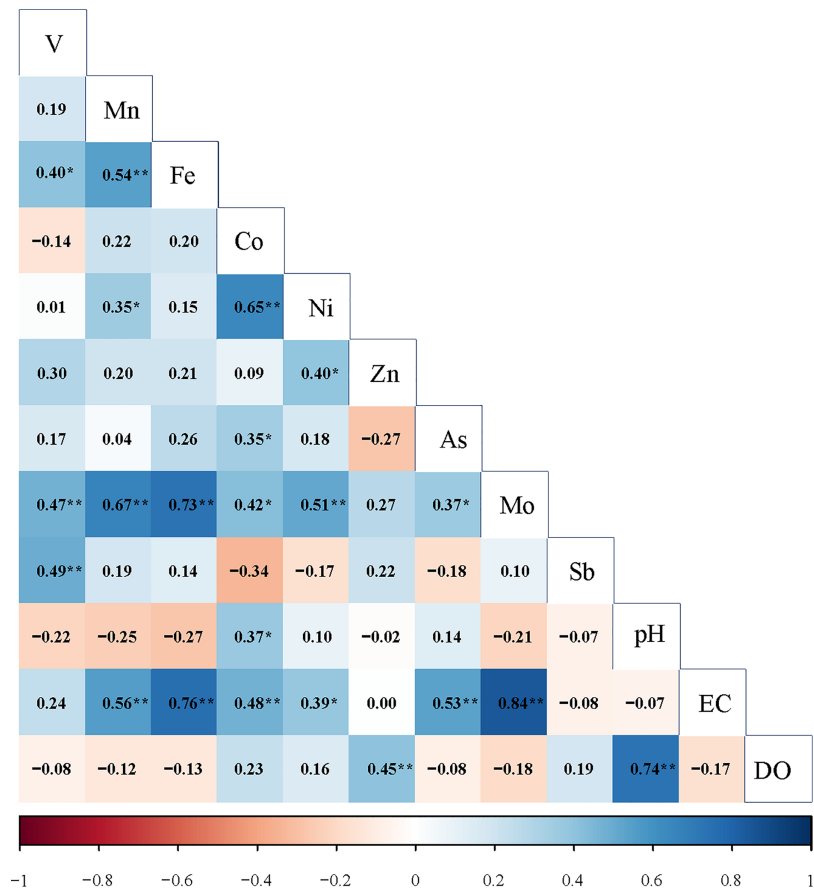


Figure 4 Correlation coefficients of heavy metals and physicochemical parameters (pH, EC and DO) in rivers in Wuhan; an asterisk (*) denotes $p < 0.05$; two asterisks (**) denotes $p < 0.01$.

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Table 3 Varimax rotated component matrix for dissolved heavy metals (the significance of KMO and Bartlett's sphericity test is <0.001).

Eigenvalues	3.74	2.11	1.19
Variance (%)	35.25	25.81	17.21
Cumulative (%)	35.25	61.07	78.27
Variable	PC1	PC2	PC3
V	0.02	0.80	0.45
Mn	0.76	0.30	0.14
Fe	0.75	0.28	0.33
Co	0.92	-0.18	0.09
Ni	0.88	-0.03	-0.03
Zn	0.27	0.78	-0.17
As	0.08	-0.29	0.84
Mo	0.58	0.29	0.66
Sb	-0.06	0.84	-0.20

Notes:

Extraction method: Principal component analysis.

Rotation method: Varimax with Kaiser normalization.

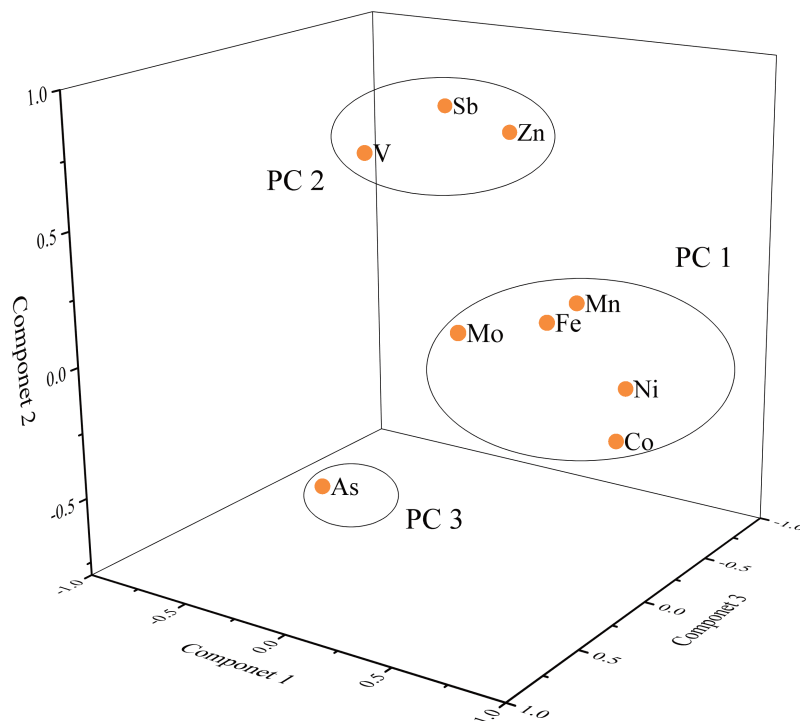


Figure 5 Loading plot of factors or dissolved heavy metals in rivers.

Full-size DOI: 10.7717/peerj.11853/fig-5

metal content in the study area. EC can measure the total dissolved metal ions in water and reflect the biogeochemistry and land use (Walker & Pan, 2006). Higher EC may lead to increased dissolved heavy metals in water (Gao et al., 2020). As shown in Fig. 4, EC was significantly positively correlated with Mn (0.557), Fe (0.757), Co (0.485), Ni (0.381), As (0.531) and Mo (0.845). The results showed that EC played an essential role in the content of dissolved heavy metals in the river.

Rainfall is an important factor in controlling dissolved heavy metals in rivers (Li & Zhang, 2010). Although it has a dilution effect in the rainy season, the amount of non-point source pollutants, mine wastewater and geological materials generated by weathering entering rivers may increase (Li & Zhang, 2010; Xu et al., 2020b). Temperature, rainfall and other factors will affect the chemical weathering of rocks (Chen et al., 2020; Ma et al., 2020; Xu et al., 2020b; Zhong et al., 2017). In the rainy season, with the increase of river flow, chemostatic behavior is induced by increasing the surface area of active minerals, which accelerates the rocks' weathering (Xu et al., 2020b; Zhong et al., 2017). Therefore, the release rate of dissolved heavy metals in carbonate rocks will increase with the acceleration of rock weathering. In addition, under high flow conditions, the solute concentrations produced by weathering of different rocks may be changed by dilution due to the decrease of water-rock interaction time (Xu et al., 2020b; Zhong et al., 2017). In our study, the low concentrations of Fe, Mn, Co, Ni and Mo could be attributed to the dilution effect at high flow, which was speculated to be derived from natural

processes. On the other hand, the relatively high concentrations of V, Zn, Sb and As could be considered the increase of anthropogenic emissions under rainfall.

Potential source identification

The sources of heavy metals are diverse, and each element may have multiple sources. CA and PCA were used to identify the sources of nine elements in our study.

CA mainly represented the correlation between two elements, and PCA can divide elements into different arrays, which indicated different anthropogenic or natural sources of these elements (Gao *et al.*, 2020; Zeng *et al.*, 2015). The higher factor explained the total variance, the higher contribution of the source to the nine elements (Li, 2007). According to the CA and PCA results, three categories could be identified for the dominant sources of nine heavy metals in Wuhan.

Group 1 defined that Mn, Fe, Co, Ni and Mo were related (Fig. 4), which indicated that their sources and behavior might originate similarly. Mn, Fe, Co, Ni and Mo presented a robust positive loading in PC1 (Fig. 5). Fe was the central element in the earth's crust and Mn, Co, Ni and Mo mainly originated from rock weathering and soil-forming processes (Li & Zhang, 2010; Xiao *et al.*, 2019; Yokoo *et al.*, 2004). Combined with significantly lower Mn, Fe and Co concentrations than the world average, we attributed group 1 to the geological source of the basin.

As shown in Table 3, V, Zn and Sb presented a strong loading in PC2 (loading values > 0.75) (Zeng, Han & Yang, 2020). V and Sb presented a significant positive correlation in Fig. 4. Moreover, V, Zn and Sb presented the same spatial distribution pattern among rivers, such as the concentrations of V, Zn and Sb in HR affected by human activities were significantly higher than those in other rivers (Wu *et al.*, 2019). A study in 2010 found that the concentrations of V and Sb were high in the upper HR, which was attributed to the input of human activities (Li & Zhang, 2010). Other studies showed that V, Zn and Sb were widely used in industry (Gao *et al.*, 2020; Kravchenko *et al.*, 2014). Therefore, though the three elements had their natural sources, we inferred that industrial emissions were the dominant factor for V, Zn and Sb in group 2.

Group 3 mainly contained As and Mo. These two metals were the main contributors to PC3 (Fig. 5) and presented a significant positive correlation (Fig. 4). The concentration of As was higher in QLR, DJR and XSR. QLR and XSR were located in the main urban area of Wuhan, and the high concentration of As might be related to urban activities. The DJR was located in the middle and lower reaches of the Yangtze River, with many plains and higher agricultural activities than other areas, so soil erosion caused by farming might be another important reason for the increase of As concentration in the water body (Wu *et al.*, 2019). The concentration of Mo was also higher in QLR and XSR, so Mo might mainly be human input of urban activities. Previous studies showed that Mo was widely used in electronics, medicine and agriculture (Elbaz-Poulichet *et al.*, 2006; Liang, 2020). Therefore, we attributed group 3 to the mixed input of urban and agricultural activities.

As described in the above analysis, Mn, Fe, Co and Ni were natural sources, while V, Zn, As and Sb were mainly anthropogenic sources. It was worth noting that Mo was

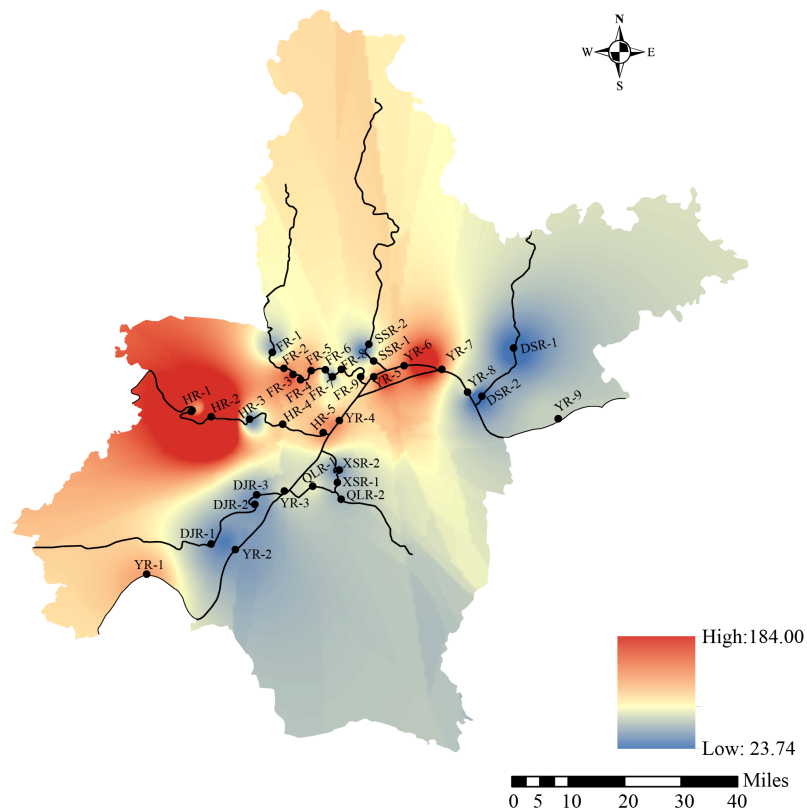


Figure 6 Spatial distribution of HPI.

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present in group 1 and group 3 simultaneously, which indicated that the natural process and human activities influenced the change of Mo in water.

Spatial distribution of heavy metal pollution index (HPI)

In this study, HPI was used for describing the potential environmental risks of heavy metals in water. It calculated the spatial trend of the HPI based on nine heavy metals in the rivers (Fig. 6). HPI ranged from 23.74 to 184.0. The HPI values of all sampling points belonged to a high level (HPI > 30), except for the two sampling points of Daoshui River. The results showed that the ecological problems of heavy metals in river water were widespread (Tiwari *et al.*, 2015). In addition, the contribution of Zn in the evaluation of HPI of rivers in Wuhan was not significant because of its lower weightage (W_i) value. Heavy metals such as Mn, Fe, Ni, As, Mo and Sb had higher weightage (W_i) values and higher HPI values, indicating that the higher concentration of these heavy metals in river water, the worse water quality (Bhaskar *et al.*, 2020). It should be noted that As and Sb contribute most of the HPI values, which was consistent with their higher concentrations in the river. The spatial distribution of HPI values showed that the ecological risk of heavy metals around HR-2 was the highest, and the HPI value of this point was 184.0, which exceeded the value of 100, which was the critical pollution index value (Bhaskar *et al.*, 2020). Overall, except for DSR-1 and DSR-2 sites, the ecological

Table 4 Hazard quotient, dermal permeability coefficient and reference dose for heavy metals in rivers in Wuhan.

	HQ _{ingestion}		HQ _{dermal}		HI		K _p ^a cm/h	RfD _{ingestion} ^{b c} μg/kg/day	RfD _{dermal} ^{b c} μg/kg/day
	Adults	Children	Adults	Children	Adults	Children			
V	5.22E-02	7.80E-02	5.45E-02	1.61E-01	1.07E-01	2.39E-01	2 × 10 ⁻³	1	0.01
Mn	1.03E-03	1.54E-03	1.35E-04	3.98E-04	1.17E-03	1.94E-03	1 × 10 ⁻³	24	0.96
Fe	5.01E-04	7.48E-04	1.31E-05	3.86E-05	5.14E-04	7.87E-04	1 × 10 ⁻³	700	140
Co	5.66E-03	8.46E-03	5.91E-05	1.74E-04	5.72E-03	8.63E-03	4 × 10 ⁻⁴	0.3	0.06
Ni	1.59E-03	2.37E-03	4.15E-05	1.22E-04	1.63E-03	2.50E-03	2 × 10 ⁻⁴	20	0.8
Zn	1.92E-04	2.87E-04	3.01E-06	8.88E-06	1.95E-04	2.96E-04	6 × 10 ⁻⁴	300	60
As	3.40E-01	5.08E-01	4.33E-03	1.28E-02	3.44E-01	5.21E-01	1 × 10 ⁻³	0.3	0.123
Mo	1.25E-02	1.87E-02	3.44E-04	1.01E-03	1.28E-02	1.97E-02	2 × 10 ⁻³	5	1.9
Sb	2.93E-01	4.38E-01	7.66E-02	2.26E-01	3.70E-01	6.64E-01	1 × 10 ⁻³	0.4	0.008

Notes:^a United States Environmental Protection Agency (2004).^b Wang et al. (2017).^c Wu et al. (2019).

risk of heavy metals in all sampling sites was a severe problem. It might be due to industrial, agricultural and domestic activities (Wang et al., 2017).

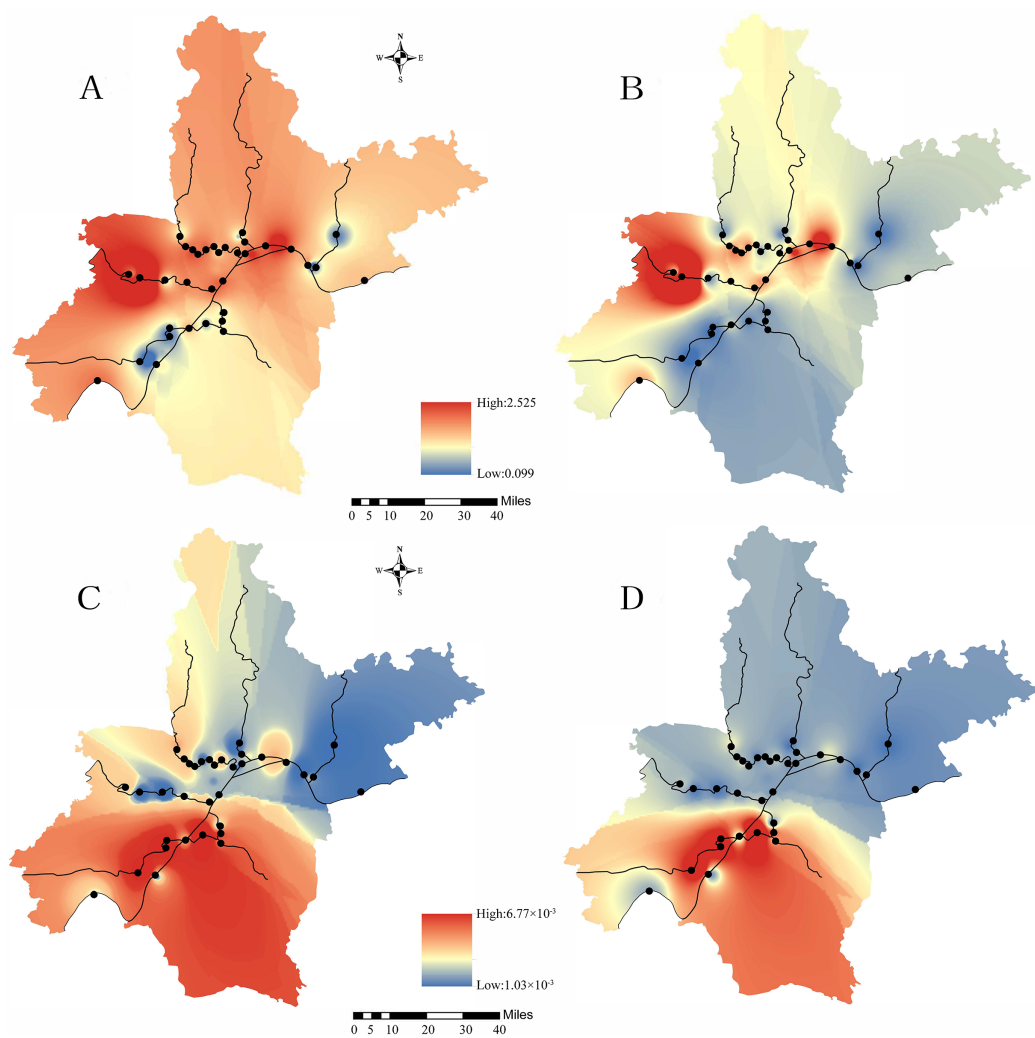
Human health risk assessment

The calculation results of HQ and HI values of heavy metals for adults and children are demonstrated in Table 4. The HQ_{ingestion}, HQ_{dermal} and HI of all heavy metals evaluated were less than the threshold 1 we considered in this study for both adults and children. Results presented that the harm of nine heavy metals in rivers of Wuhan to residents was low. Moreover, we observed that children had higher HQ_{ingestion} and HQ_{dermal} than adults, indicating that heavy metals were more harmful to children. It was worth noting that the HI values of Sb, As and V were at least one order of magnitude higher than other heavy metals. Therefore, human health monitoring and environmental supervision agencies should pay special attention to the sources and exposure routes of Sb, As and V in rivers in Wuhan.

The HI values of V and Sb and the CR values of As and their spatial distribution are shown in Table 5 and Fig. 7. For adults and children, the order of HI values of V in the rivers was HR>QLR>FR>XSR>YR>DJR>SSR>DSR, and the high-risk areas were HR, QLR, FR and XSR. The order of HI values of Sb was YR>HR>FR>SSR>XSR>QLR>DSR>DJR, and the high-risk areas were YR, HR, FR and SSR. In addition, the HI value in YR (0.843 for children), HR (0.808 for children) and FR (0.732 for children) were relatively close to 1. Therefore, Sb might have potential non-carcinogenic to human health, especially in the areas around the HR-2, YR-6, YR-7 and FR-3 (Figs. 7A and 7B). The HI value of As for children in QLR exceeded threshold 1, and that of adults was relatively close to 1. Moreover, the HI values of As in DJR (0.586 for adults, 0.886 for children) were relatively close to 1. Therefore, As might have potential non-carcinogenic risk to adults and children in these areas. The order of CR value of As in the rivers was QLR>DJR>XSR>HR>FH>YR>SSR>DSR. The CR values of As all exceeded the target risk (10⁻⁴) (Chen & Liao, 2006; Qu et al., 2018),

Table 5 The HI values of V, Sb and As and CR values of As in rivers in Wuhan.

	V(HI)		Sb(HI)		As(HI)		As(CR)	
	Adults	Children	Adults	Children	Adults	Children	Adults	Children
Yangtze River	9.95E-02	2.23E-01	4.65E-01	8.34E-01	2.78E-01	4.21E-01	1.24E-03	1.85E-03
Dongjin River	7.21E-02	1.61E-01	1.31E-01	2.36E-01	5.86E-01	8.86E-01	2.60E-03	3.88E-03
Qingling River	1.11E-01	2.49E-01	2.07E-01	3.72E-01	7.21E-01	1.09E+00	3.20E-03	4.77E-03
Xunsi River	1.05E-01	2.35E-01	2.27E-01	4.07E-01	3.75E-01	5.67E-01	1.66E-03	2.48E-03
Han River	1.72E-01	3.85E-01	4.50E-01	8.08E-01	2.91E-01	4.40E-01	1.29E-03	1.93E-03
Fu River	1.10E-01	2.47E-01	4.08E-01	7.32E-01	2.90E-01	4.39E-01	1.29E-03	1.93E-03
Sheshui River	7.18E-02	1.61E-01	2.94E-01	5.28E-01	2.67E-01	4.04E-01	1.19E-03	1.77E-03
Daoshui River	6.00E-02	1.34E-01	1.36E-01	2.45E-01	2.59E-01	3.91E-01	1.15E-03	1.71E-03

**Figure 7** Spatial distribution of HI for Sb (A and B) and CR for As (C and D). (A), (C) Children; (B), (D) Adults. Full-size [DOI: 10.7717/peerj.11853/fig-7](https://doi.org/10.7717/peerj.11853/fig-7)

which indicated that the carcinogenic risk of As to adults and children was widespread in the study area. Spatially, the areas around QLR-1 and DJR-1 have the highest risk (Figs. 7C and 7D). These findings deserve our grave concern about the carcinogenic effects of As in rivers in Wuhan.

According to the comprehensive results of the HI and CR index, the high-risk areas of rivers in Wuhan were summarized as follows: (1) As pollution was a significant threat to human health and the high-risk areas were QLR and DJR. (2) The high-risk areas of V were HR, QLR, FR and XSR, especially in HR, QLR-1 and XSR-1. (3) The high-risk areas of Sb were YR, HR and FR, especially in YR-6, YR-7 and HR-2.

According to the risk assessment results, As and Sb were the primary pollutants in rivers in Wuhan, which were consistent with the comparison results of drinking water standards (Table 2). The side effects of heavy metals have been widely reported, such as V has a toxic impact on the human digestive system, blood, nervous system and immune system (Chlubek et al., 2012; Rawal et al., 1997). Sb may cause discomforts such as nausea, vomiting, anorexia, abdominal pain and gastric ulcer (Saerens et al., 2019; Sundar & Chakravarty, 2010). Moreover, excessive As intake may cause cancers (liver cancer, lung cancer, bladder cancer) and other side effects (hypertension, neuropathy, diabetes, tibial disease) (Wu et al., 2009b; Xu & Wang, 2020). Therefore, we should pay special attention to the potential non-carcinogenic risk of V and Sb and the potential carcinogenic risk of As. It is necessary to take relevant measures to prevent excessive heavy metals from entering rivers, and maintain a healthy water ecosystem and provide water resources guarantee for the economic development of Wuhan.

However, there was uncertainty in the description of health risks for heavy metals, which had been pointed out by US EPA and other relevant studies (Qu et al., 2018; United States Environmental Protection Agency, 2009; Wu et al., 2009b). Water and skin contact factor (K_p), different exposure conditions caused by different ages and receptors, temporal changes of pollutant concentration and daily water intake cannot be quantified, which led to methodological uncertainty. Furthermore, the US EPA is the primary source of parameters in this study, which might not apply to the Chinese. Consequently, it is necessary to clarify the risk characteristics further and improve the risk assessment method by investigating river risk levels in Wuhan.

CONCLUSIONS

The spatial distribution of dissolved heavy metals in Wuhan had great spatial heterogeneity. Different distribution characteristics of dissolved heavy metals caused by human activities (industrial, agricultural, domestic) in different regions of Wuhan. The results of CA and PCA showed that Mn, Fe, Co, Ni and Mo were attributed to the geological sources of the basin, and V, Zn and Sb were controlled by industrial activities, while As was mainly dominated by the mixed input of urban and agricultural activities.

In general, the concentrations of all heavy metals in Wuhan river water were within the standard range of China's drinking water. However, Sb in YR and HR exceeded the drinking water guidelines set by WHO, US EPA and China EPA, and As in DJR and QLR were close to the three drinking water guidelines, which required special attention.

The heavy metal pollution index results showed that As and Sb contributed most of the HPI values, which was consistent with high concentrations in the rivers, indicating that these two heavy metals' ecological risk was high. Non-carcinogenic risk and carcinogenic risk of heavy metals were analyzed by HI and CR. The results showed that V and Sb had potential non-carcinogenic risk and As might have a potential carcinogenic risk to adults and children in the study area, while As might have a potential non-carcinogenic risk for children around QLR. The results showed that As and Sb were the primary pollutants in rivers in Wuhan. We should prevent them from damaging the aquatic ecosystem and provide water resources guarantee for the economic development of Wuhan. It is necessary to develop a long-term monitoring scheme for As and Sb, which can effectively control and manage the As and Sb pollution in rivers in the corresponding areas.

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ADDITIONAL INFORMATION AND DECLARATIONS

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Competing Interests

The authors declare that they have no competing interests.

Author Contributions

- Xingyong Zhang conceived and designed the experiments, performed the experiments, analyzed the data, prepared figures and/or tables, authored or reviewed drafts of the paper, and approved the final draft.

- Qixin Wu conceived and designed the experiments, authored or reviewed drafts of the paper, and approved the final draft.
- Shilin Gao performed the experiments, authored or reviewed drafts of the paper, and approved the final draft.
- Zhuhong Wang conceived and designed the experiments, authored or reviewed drafts of the paper, and approved the final draft.
- Shouyang He analyzed the data, authored or reviewed drafts of the paper, and approved the final draft.

Data Availability

The following information was supplied regarding data availability:

Data of measured dissolved heavy metal concentrations, physicochemical characteristics, and date of sampling are available in the [Supplemental Files](#).

Supplemental Information

Supplemental information for this article can be found online at <http://dx.doi.org/10.7717/peerj.11853#supplemental-information>.

REFERENCES

- Ali MM, Ali ML, Islam MS, Rahman MZ. 2016. Preliminary assessment of heavy metals in water and sediment of Karnaphuli River. *Bangladesh Environmental Nanotechnology, Monitoring & Management* 5(12):27–35 DOI 10.1016/j.enmm.2016.01.002.
- Antoniadis V, Shaheen SM, Boersch J, Frohne T, Laing GD, Rinklebe J. 2016. Bioavailability and risk assessment of potentially toxic elements in garden edible vegetables and soils around a highly contaminated former mining area in Germany. *Journal of Environmental Management* 186(2):192–200 DOI 10.1016/j.jenvman.2016.04.036.
- Bhaskar M, Dixit AK, Ojha KK, Dubey S, Singh A, Abhishek A. 2020. The impact of anthropogenic organic and inorganic pollutants on the Hasdeo River Water Quality in Korba Region, Chhattisgarh, India. *Bioinformation* 16(4):332–340 DOI 10.6026/97320630016332.
- Cameron H, Mata MT, Riquelme C. 2018. The effect of heavy metals on the viability of *Tetraselmis marina* AC16-MESO and an evaluation of the potential use of this microalga in bioremediation. *PeerJ* 6(4):e5295 DOI 10.7717/peerj.5295.
- Chen B-B, Li S-L, Pogge von Strandmann PAE, Sun J, Zhong J, Li C, Ma T-T, Xu S, Liu C-Q. 2020. Ca isotope constraints on chemical weathering processes: evidence from headwater in the Changjiang River, China. *Chemical Geology* 531(16):119341 DOI 10.1016/j.chemgeo.2019.119341.
- Chen K, Jiao JJ, Huang J, Huang R. 2007. Multivariate statistical evaluation of trace elements in groundwater in a coastal area in Shenzhen. *China Environmental Pollution* 147(3):771–780 DOI 10.1016/j.envpol.2006.09.002.
- Chen SC, Liao CM. 2006. Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. *Science of The Total Environment* 366(1):112–123 DOI 10.1016/j.scitotenv.2005.08.047.
- China EPA. 2002. Environmental quality standards for surface water (GB 3838-2002). Available at http://kjs.mee.gov.cn/hjbhzbz/bzwb/shjbh/shjzlbz/200206/t20020601_66497.shtml.
- China EPA. 2006. Environmental quality standards for drinking water quality (GB 5749-2006). Available at <http://www.nhfpc.gov.cn/wjw/pgw/201212/33644.shtml>.

- Chlubek D, Gutowska I, Baranowska-Bosiacka I, Korbecki J. 2012.** Biochemical and medical importance of vanadium compounds. *Acta Biochimica Polonica* **59**:2138 DOI 10.18388/abp.2012_2138.
- Chowdhury S, Mazumder MAJ, Al-Attas O, Husain T. 2016.** Heavy metals in drinking water: occurrences, implications, and future needs in developing countries. *Science of The Total Environment* **569–570(2)**:476–488 DOI 10.1016/j.scitotenv.2016.06.166.
- Dong Z, Kang S, Qin X, Li X, Qin D, Ren J. 2015.** New insights into trace elements deposition in the snow packs at remote alpine glaciers in the northern Tibetan Plateau, China. *Science of The Total Environment* **529(15)**:101–113 DOI 10.1016/j.scitotenv.2015.05.065.
- Du W, Li A, Lu M, An K, Fan J. 2014.** Preliminary health risk assessment of heavy metals in the Yangtze River of Wuhan Area. *Environmental Science & Technology* **37**:535–539.
- Elbaz-Poulichet F, Seidel JL, Casiot C, Tusseau-Vuillemin MH. 2006.** Short-term variability of dissolved trace element concentrations in the Marne and Seine rivers near Paris. *Science of The Total Environment* **367(1)**:278–287 DOI 10.1016/j.scitotenv.2005.11.009.
- Eneji IS, Sha’Ato R, Annune PA. 2012.** An assessment of heavy metals loading in River Benue in the Makurdi metropolitan area in Central Nigeria. *Environmental Monitoring and Assessment* **184(1)**:201–207 DOI 10.1007/s10661-011-1959-0.
- Environmental Protection Administration of China. 2003.** National primary drinking water regulations. Available at <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations>.
- Gaillardet J, Viers J, Dupré B. 2014.** Trace elements in river waters. *Treatise on Geochemistry* **195–235(13)**:195–235 DOI 10.1016/B978-0-08-095975-7.00507-6.
- Gao S, Wang Z, Wu Q, Zeng J. 2020.** Multivariate statistical evaluation of dissolved heavy metals and a water quality assessment in the Lake Aha watershed, Southwest China. *PeerJ* **8**:e9660 DOI 10.7717/peerj.9660.
- Giri S, Singh AK. 2014.** Risk assessment, statistical source identification and seasonal fluctuation of dissolved metals in the Subarnarekha River, India. *Journal of Hazardous Materials* **265(3)**:305–314 DOI 10.1016/j.jhazmat.2013.09.067.
- Gong X, Xiao L, Zhao Z, Li Q, Feng F, Zhang L, Deng Z. 2018.** Spatial variation of polycyclic aromatic hydrocarbons (PAHs) in surface sediments from rivers in hilly regions of Southern China in the wet and dry seasons. *Ecotoxicology and Environmental Safety* **156**:322–329 DOI 10.1016/j.ecoenv.2018.03.004.
- Guan S, Meng H, Zhou M. 2008.** The Distribution and growing Ruels of Karst in Wuhan. *Urban Geotechnical Investigation & Surveying* **4**:145–149.
- Gupta M, Srivastava PK. 2010.** Integrating GIS and remote sensing for identification of groundwater potential zones in the hilly terrain of Pavagarh, Gujarat, India. *Water International* **35(2)**:233–245 DOI 10.1080/02508061003664419.
- Han G, Liu C-Q. 2004.** Water geochemistry controlled by carbonate dissolution: a study of the river waters draining karst-dominated terrain, Guizhou Province, China. *Chemical Geology* **204(1–2)**:1–21 DOI 10.1016/j.chemgeo.2003.09.009.
- Han G, Song Z, Tang Y, Wu Q, Wang Z. 2019.** Ca and Sr isotope compositions of rainwater from Guiyang city, Southwest China: Implication for the sources of atmospheric aerosols and their seasonal variations. *Atmospheric Environment* **214(5482)**:116854 DOI 10.1016/j.atmosenv.2019.116854.
- Helena B. 2000.** Temporal evolution of groundwater composition in an alluvial aquifer (Pisuerga River, Spain) by principal component analysis. *Water Research* **34(3)**:807–816 DOI 10.1016/S0043-1354(99)00225-0.

- Hu Y, Qi S, Wu C, Ke Y, Chen J, Chen W, Gong X. 2012. Preliminary assessment of heavy metal contamination in surface water and sediments from Honghu Lake, East Central China. *Frontiers of Earth Science* 6(1):39–47 DOI 10.1007/s11707-012-0309-z.
- Jiang H, Qin D, Chen Z, Tang S, Bai S, Mou Z. 2016. Heavy metal levels in fish from heilongjiang river and potential health risk assessment. *Bulletin of Environmental Contamination and Toxicology* 97:536–542.
- Kowalkowski T, Zbytniewski R, Szejna J, Buszewski B. 2006. Application of chemometrics in river water classification. *Water Research* 40(4):744–752 DOI 10.1016/j.watres.2005.11.042.
- Kravchenko J, Darrah TH, Miller RK, Lyerly HK, Vengosh A. 2014. A review of the health impacts of barium from natural and anthropogenic exposure. *Environmental Geochemistry and Health* 36(4):797–814 DOI 10.1007/s10653-014-9622-7.
- Krishna AK, Satyanarayanan M, Govil PK. 2009. Assessment of heavy metal pollution in water using multivariate statistical techniques in an industrial area: a case study from Patancheru, Medak District, Andhra Pradesh, India. *Journal of Hazardous Materials* 167(1–3):366–373 DOI 10.1016/j.jhazmat.2008.12.131.
- Krishnamurti G, Subashchandrabose SR, Megharaj M, Naidu R. 2015. Assessment of bioavailability of heavy metal pollutants using soil isolates of *Chlorella* sp.. *Environmental Science and Pollution Research International* 22(12):8826–8832.
- Kumar M, Ramanathan AL, Tripathi R, Farswan S, Kumar D, Bhattacharya P. 2017. A study of trace element contamination using multivariate statistical techniques and health risk assessment in groundwater of Chhaprola Industrial Area, Gautam Buddha Nagar, Uttar Pradesh, India. *Chemosphere* 166(185):135–145 DOI 10.1016/j.chemosphere.2016.09.086.
- Lemly AD. 1996. Evaluation of the hazard quotient method for risk assessment of selenium. *Ecotoxicology and Environmental Safety* 35(2):156–162 DOI 10.1006/eesa.1996.0095.
- Li P. 2019. Analysis on black and odorous water treatment of Xunsi River in Wuhan. *Energy Conservation and Environmental Protection* 6:125.
- Li S, Zhang Q. 2010. Risk assessment and seasonal variations of dissolved trace elements and heavy metals in the Upper Han River, China. *China Journal of Hazardous Materials* 181(1–3):1051–1058 DOI 10.1016/j.jhazmat.2010.05.120.
- Li X. 2007. Comparison and application of principal component analysis, factor analysis and cluster analysis. *Journal of Shandong Institute of Education* 6:23–26 DOI 10.3969/j.issn.1008-2816.2007.06.006.
- Liang Y. 2020. *Study on removal of heavy metal molybdenum in water by precipitation method*. Henan: Henan Science Technology, 130–132.
- Liu J, Han G. 2021. Tracing riverine particulate black carbon sources in Xijiang river basin: insight from stable isotopic composition and Bayesian mixing model.. *Water Research* 194:116932.
- Loska K, Wiechula D. 2003. Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik reservoir. *Chemosphere* 51(8):723–733 DOI 10.1016/S0045-6535(03)00187-5.
- Ma T, Weynell M, Li S-L, Liu Y, Chetelat B, Zhong J, Xu S, Liu C-Q. 2020. Lithium isotope compositions of the Yangtze River headwaters: weathering in high-relief catchments. *Geochimica Et Cosmochimica Acta* 280(8):46–65 DOI 10.1016/j.gca.2020.03.029.
- Markich SJ, Brown PL. 1998. Relative importance of natural and anthropogenic influences on the fresh surface water chemistry of the Hawkesbury–Nepean River, south-eastern Australia. *Science of the Total Environment* 217(3):201–230 DOI 10.1016/S0048-9697(98)00188-0.
- Meng Q, Zhang J, Zhang Z, Wu T. 2016. Geochemistry of dissolved trace elements and heavy metals in the Dan River Drainage (China): distribution, sources, and water quality assessment.

- Environmental Science and Pollution Research* **23(8)**:8091–8103
DOI [10.1007/s11356-016-6074-x](https://doi.org/10.1007/s11356-016-6074-x).
- Mohan SV, Nithila P, Reddy SJ. 2008.** Estimation of heavy metals in drinking water and development of heavy metal pollution index. *Journal of Environmental Science and Health Part A: Environmental Science and Engineering and Toxicology* **31(2)**:283–289
DOI [10.1080/10934529609376357](https://doi.org/10.1080/10934529609376357).
- Nasrabadi T. 2015.** An index approach to metallic pollution in river waters. *International Journal of Environmental Research* **9**:385–394.
- Obiri S, Dodoo DK, Okai-Sam F, Essumang DK. 2006.** Cancer health risk assessment of exposure to arsenic by workers of AngloGold Ashanti-Obuasi gold mine. *Bulletin of Environmental Contamination and Toxicology* **76(2)**:195–201 DOI [10.1007/s00128-006-0907-0](https://doi.org/10.1007/s00128-006-0907-0).
- Papafilippaki AK, Kotti ME, Stavroulakis GG. 2008.** Seasonal variations in dissolved heavy metals in the Keritis river, Chania, Greece. *Global Nest Journal* **10**:320–325.
- Qu L, Huang H, Xia F, Liu Y, Dahlgren RA, Zhang M, Mei K. 2018.** Risk analysis of heavy metal concentration in surface waters across the rural-urban interface of the Wen-Rui Tang River, China. *Environmental Pollution* **237**:639–649 DOI [10.1016/j.envpol.2018.02.020](https://doi.org/10.1016/j.envpol.2018.02.020).
- Rawal SB, Singh MV, Salhan A, Selvamurthy W, Tyagi AK, Kumar S. 1997.** Influence of vanadium on acclimatization of humans to high altitude. *International Journal of Biometeorology* **40(2)**:95–98 DOI [10.1007/s004840050025](https://doi.org/10.1007/s004840050025).
- Saerens A, Ghosh M, Verdonck J, Godderis L. 2019.** Risk of cancer for workers exposed to antimony compounds: a systematic review. *International Journal of Environmental Research and Public Health* **16(22)**:4474 DOI [10.3390/ijerph16224474](https://doi.org/10.3390/ijerph16224474).
- Sundar S, Chakravarty J. 2010.** Antimony toxicity. *International Journal of Environmental Research and Public Health* **7(12)**:4267–4277 DOI [10.3390/ijerph7124267](https://doi.org/10.3390/ijerph7124267).
- Thuong NT, Yoneda M, Ikegami M, Takakura M. 2013.** Source discrimination of heavy metals in sediment and water of To Lich River in Hanoi City using multivariate statistical approaches. *Environmental Monitoring and Assessment* **185(10)**:8065–8075
DOI [10.1007/s10661-013-3155-x](https://doi.org/10.1007/s10661-013-3155-x).
- Tiwari AK, De Maio M, Singh PK, Mahato MK. 2015.** Evaluation of surface water quality by using GIS and a Heavy Metal Pollution Index (HPI) model in a coal mining area, India. *Bulletin of Environmental Contamination and Toxicology* **95(3)**:304–310 DOI [10.1007/s00128-015-1558-9](https://doi.org/10.1007/s00128-015-1558-9).
- Tripathee L, Kang S, Sharma CM, Rupakheti D, Paudyal R, Huang J, Sillanpaa M. 2016.** Preliminary health risk assessment of potentially toxic metals in surface water of the Himalayan rivers, Nepal. *Bulletin of Environmental Contamination and Toxicology* **97(6)**:855–862
DOI [10.1007/s00128-016-1945-x](https://doi.org/10.1007/s00128-016-1945-x).
- United States Environmental Protection Agency. 2004.** Risk assessment: “supplemental guidance for dermal risk assessment”. Part E of risk assessment guidance for superfund, human health evaluation manual. Vol. I. Available at <https://www.epa.gov/risk/risk-assessment-guidance-superfund-rags-part-e>.
- United States Environmental Protection Agency. 2009.** *Risk Assessment guidance for superfund (RAGS): human health evaluation manual (Part E, supplemental guidance for dermal risk assessment) interim*. Vol. I. Washington, D.C.: US EPA.
- Varol M. 2011.** Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *Journal of Hazardous Materials* **195(1/2)**:355–364 DOI [10.1016/j.jhazmat.2011.08.051](https://doi.org/10.1016/j.jhazmat.2011.08.051).

- Varol M, Şen B. 2012.** Assessment of nutrient and heavy metal contamination in surface water and sediments of the upper Tigris River, Turkey. *Catena* **92**(1/2):1–10 DOI [10.1016/j.catena.2011.11.011](https://doi.org/10.1016/j.catena.2011.11.011).
- Waalkes MP. 2000.** Cadmium carcinogenesis in review. *Journal of Inorganic Biochemistry* **79**(1–4):241–244 DOI [10.1016/S0162-0134\(00\)00009-X](https://doi.org/10.1016/S0162-0134(00)00009-X).
- Walker CE, Pan Y. 2006.** Using diatom assemblages to assess urban stream conditions. *Hydrobiologia* **561**(1):179–189 DOI [10.1007/s10750-005-1613-3](https://doi.org/10.1007/s10750-005-1613-3).
- Wanda EMM, Gulula LC, Phiri G. 2012.** Determination of characteristics and drinking water quality index in Mzuzu City, Northern Malawi. *Physics and Chemistry of the Earth, Parts A/B/C* **50–52**(10):92–97 DOI [10.1016/j.pce.2012.09.004](https://doi.org/10.1016/j.pce.2012.09.004).
- Wang J, Liu G, Liu H, Lam PKS. 2017.** Multivariate statistical evaluation of dissolved trace elements and a water quality assessment in the middle reaches of Huaihe River, Anhui, China. *Science of The Total Environment* **583**(7):421–431 DOI [10.1016/j.scitotenv.2017.01.088](https://doi.org/10.1016/j.scitotenv.2017.01.088).
- Warnken KW, Santschi PH. 2009.** Delivery of trace metals (Al, Fe, Mn, V, Co, Ni, Cu, Cd, Ag, Pb) from the Trinity river watershed towards the ocean. *Estuaries and Coasts* **32**(1):158–172 DOI [10.1007/s12237-008-9088-x](https://doi.org/10.1007/s12237-008-9088-x).
- WHO. 2011.** *Guidelines for drinking-water quality*. Fourth Edition. Geneva: World Health Organization.
- Wu B, Zhang X, Zhang X, Yasun A, Zhang Y, Zhao D, Ford T, Cheng S. 2009a.** Semi-volatile organic compounds and trace elements in the Yangtze River source of drinking water. *Ecotoxicology* **18**(6):707–714 DOI [10.1007/s10646-009-0331-4](https://doi.org/10.1007/s10646-009-0331-4).
- Wu B, Zhao DY, Jia HY, Zhang Y, Zhang XX, Cheng SP. 2009b.** Preliminary risk assessment of trace metal pollution in surface water from Yangtze River in Nanjing Section, China. *Bulletin of Environmental Contamination and Toxicology* **82**(4):405–409 DOI [10.1007/s00128-008-9497-3](https://doi.org/10.1007/s00128-008-9497-3).
- Wu WT, Ran XB, Li JX, Wang H, Li ML, Liu J, Zang JY. 2019.** Sources, distribution, and fluxes of major and trace elements in the Yangtze River. *Huan Jing Ke Xue* **40**:4900–4913 DOI [10.13227/j.hj.kx.201903134](https://doi.org/10.13227/j.hj.kx.201903134).
- Xiao J, Jin Z, Wang J. 2014.** Geochemistry of trace elements and water quality assessment of natural water within the Tarim River Basin in the extreme arid region, NW China. *Journal of Geochemical Exploration* **136**:118–126 DOI [10.1016/j.gexplo.2013.10.013](https://doi.org/10.1016/j.gexplo.2013.10.013).
- Xiao J, Wang L, Deng L, Jin Z. 2019.** Characteristics, sources, water quality and health risk assessment of trace elements in river water and well water in the Chinese Loess Plateau. *Science of The Total Environment* **650**:2004–2012 DOI [10.1016/j.scitotenv.2018.09.322](https://doi.org/10.1016/j.scitotenv.2018.09.322).
- Xu, Wang. 2020.** Wuhan water resources bulletin. Available at http://swjwuhangovcn/szy/202011/t20201126_1518840.html.
- Xu J, Zheng L, Xu L, Liu B, Liu J, Wang X. 2020a.** Identification of dissolved metal contamination of major rivers in the southeastern hilly area, China: distribution, source apportionment, and health risk assessment. *Environmental Science and Pollution Research* **27**(4):3908–3922 DOI [10.1007/s11356-019-06774-8](https://doi.org/10.1007/s11356-019-06774-8).
- Xu S, Lang Y, Zhong J, Xiao M, Ding H. 2020b.** Coupled controls of climate, lithology and land use on dissolved trace elements in a Karst river system. *Journal of Hydrology* **591**(2):125328 DOI [10.1016/j.jhydrol.2020.125328](https://doi.org/10.1016/j.jhydrol.2020.125328).
- Yang F, Hao Z, Zhang S, Liu H, Wang C, Ling Q. 2016.** Environment geochemistry of heavy metals in the alluvial soils of Yangtze river in Wuhan City. *Acta Geologica Sinica* **90**:1955–1964.
- Yi Y, Yang Z, Zhang S. 2011.** Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. *Environmental Pollution* **159**(10):2575–2585 DOI [10.1016/j.envpol.2011.06.011](https://doi.org/10.1016/j.envpol.2011.06.011).

- Yokoo Y, Nakano T, Nishikawa M, Quan H. 2004.** Mineralogical variation of Sr-Nd isotopic and elemental compositions in loess and desert sand from the central Loess Plateau in China as a provenance tracer of wet and dry deposition in the northwestern Pacific. *Chemical Geology* **204**(1–2):45–62 DOI [10.1016/j.chemgeo.2003.11.004](https://doi.org/10.1016/j.chemgeo.2003.11.004).
- Zaric NM, Deljanin I, Ilijevic K, Stanisavljevic L, Ristic M, Grzetic I. 2018.** Assessment of spatial and temporal variations in trace element concentrations using honeybees (*Apis mellifera*) as bioindicators. *PeerJ* **6**(6):e5197 DOI [10.7717/peerj.5197](https://doi.org/10.7717/peerj.5197).
- Zeng J, Han G. 2020a.** Preliminary copper isotope study on particulate matter in Zhujiang River, southwest China: application for source identification. *Ecotoxicology and Environmental Safety* **198**:110663 DOI [10.1016/j.ecoenv.2020.110663](https://doi.org/10.1016/j.ecoenv.2020.110663).
- Zeng J, Han G. 2020b.** Tracing zinc sources with Zn isotope of fluvial suspended particulate matter in Zhujiang River, southwest China. *Ecological Indicators* **118**:106723 DOI [10.1016/j.ecolind.2020.106723](https://doi.org/10.1016/j.ecolind.2020.106723).
- Zeng J, Han G, Wu Q, Tang Y. 2019.** Geochemical characteristics of dissolved heavy metals in Zhujiang River, Southwest China: spatial-temporal distribution, source, export flux estimation, and a water quality assessment. *PeerJ* **7**(11):e6578 DOI [10.7717/peerj.6578](https://doi.org/10.7717/peerj.6578).
- Zeng J, Han G, Yang K. 2020.** Assessment and sources of heavy metals in suspended particulate matter in a tropical catchment, northeast Thailand. *Journal of Cleaner Production* **265**:121898 DOI [10.1016/j.jclepro.2020.121898](https://doi.org/10.1016/j.jclepro.2020.121898).
- Zeng X, Liu Y, You S, Zeng G, Tan X, Hu X, Hu X, Huang L, Li F. 2015.** Spatial distribution, health risk assessment and statistical source identification of the trace elements in surface water from the Xiangjiang River, China. *Environmental Science and Pollution Research* **22**(12):9400–9412 DOI [10.1007/s11356-014-4064-4](https://doi.org/10.1007/s11356-014-4064-4).
- Zhang Z, Lu Y, Li H, Tu Y, Liu B, Yang Z. 2018.** Assessment of heavy metal contamination, distribution and source identification in the sediments from the Ziji River, China. *Science of The Total Environment* **645**(8):235–243 DOI [10.1016/j.scitotenv.2018.07.026](https://doi.org/10.1016/j.scitotenv.2018.07.026).
- Zhong J, Li SL, Tao F, Yue F, Liu CQ. 2017.** Sensitivity of chemical weathering and dissolved carbon dynamics to hydrological conditions in a typical Karst river. *Scientific Reports* **7**(1):42944 DOI [10.1038/srep42944](https://doi.org/10.1038/srep42944).