Distribution, assessment, and source of heavy metals in sediments of the Qinjiang River, China

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Abstract:

Heavy metals are toxic, persistent and non-degradable. After sedimentation and adsorption, they accumulate in water sediments. The aim of this study was to understand the heavy metal pollution of Qinjiang River sediments on the ecological environment and apportioning sources. The mean total concentrations of Mn, Zn, Cr, Cu, and Pb are 3.14, 2.33, 1.39, 5.79, and 1.33 times higher than the background values, respectively, except for the Co, Ni, and Cd, which are lower than the background values; Fe, Co, Ni, Cd, Cr, Cu, and Pb are all primarily in the residual state, while Mn and Zn are primarily in the acid-soluble and oxidizable states, respectively. I_{geo}, RI, SQGs and RAC together indicate that the pollution status and ecological risk of heavy metals in Qinjiang River sediments are generally moderate; among them, Fe, Co, Ni, Cd, Cr, and Pb are not harmful to the ecological environment of the Qinjiang River. Cu is not readily released because of its higher residual composition, depicting that Cu is less harmful to the ecological environment. Mn and Zn, as the primary pollution factors of the Qinjiang River, are harmful to the ecological environment. This heavy metal pollution in surface sediments of the Qinjiang River primarily comes from manganese and zinc ore mining. Manganese carbonate and its weathered secondary manganese oxide are frequently associated with a significant amount of residual copper and Cd, as a higher pH is suitable for the deposition and enrichment of these heavy metals. Lead-zinc ore and its weathering products form organic compounds with residual Fe, Co, Cr, and Ni, and their content is related to salinity. The risk assessment results of heavy metals in sediments provide an important theoretical basis for the prevention and control of heavy metal pollution in Qinjiang River.

Keywords: Heavy metals; Risk assessment; Source analysis; Surface sediment; Qinjiang River

1. Introduction

Sediments are a crucial part of rivers, lakes, etc. During several physical and chemical processes, suspended solids and different ions in the water are adsorbed and enriched in sediments in river channels, clarifying the contamination in water sediments (El Zokm et al. 2015, Okbah et al. 2005). It can objectively show the area's water quality. Unlike other pollutants in water bodies, heavy metal contaminants cannot be efficiently eliminated by natural decomposition processes, but they instead accumulate in sediments in different ways (Rahman et al. 2014, Zhang et al. 2009). In most cases, more than 95% of heavy metals in water bodies are eliminated and stored in sediments in various forms (Abrahim & Parker 2008, Gao & Chen 2012). Thus, there is a continuous accumulation process of heavy metals in sediments. The sediments in the water body are the "sinks" of heavy metal pollutants in the water body (Ciszewski & Grygar 2016, Shotbolt et al. 2005). Simultaneously, when the environmental medium conditions (like pH, Eh) change, the heavy metals in the sediments can be released into the water body and become the water body's "secondary pollution source" (Chapman et al. 2013, Gu et al. 2014, Nielsen et al. 2010). Heavy metals in the bottom sediments of water bodies have the characteristics of extensive sources, simple accumulation, long residual time, and are difficult to detect after pollution (Luo et al. 2021, Zhou et al. 2020). Generally, heavy metals in sediments are present in various fractions (acid-soluble, reducible, oxidizable, and residual) (Morillo et al. 2002, Zhang et al. 2012), and the fractions' content influences the heavy metals' bioavailability; for example, the residual is more stable and less likely to be released. Thus, the total concentrations of heavy metals in sediments do not exactly show the environmental pollution status. Additionally, it must be determined in combination with the geochemical fractions of heavy metals in sediments (Krupadam et al. 2006, Marcovecchio & Ferrer 2005).

Qinzhou City is located in the southernmost part of the Qinhang metallogenic belt (Jingwen et al. 2013). There are several ilmenite, manganese, and lead-zinc ore fields in Qinzhou. Medium-sized and large metal ores include Xinhua lead-zinc ore in Pubei, Huarong-Dadong manganese ore, and Nahualing manganese ore in Qinnan District (Hu et al. 2017). With the implementation of regional economic development policies, including the Belt and Road Initiative, free trade zones, and world-class petrochemical industrial parks, Qinzhou's economy has rapidly developed, and the degree of industrialization and urbanization has been continuously promoted, bringing extensive pressure on environmental quality (Xia et al. 2011, Zhang et al. 2014, Zheng et al. 2012). Recently, the monitoring sections' water quality in the Qinjiang River is usually classified as inferior V, and the water quality is seriously polluted. However, few studies have focused on the ecological risks of sediment pollution in the Qinjiang River; therefore, it is urgent and crucial to perform research work related to heavy metal pollution in Qinjiang River sediments.

This study primarily addresses the environmental pollution levels and feasible sources of heavy metals (Fe, Mn, Zn, Co, Ni, Cd, Cr, Cu, and Pb) in the sediments of the Qinjiang River. The heavy metals are categorized into four different fractions using the improved BCR-sequential extraction method, and then the ecological risk is evaluated using geo-accumulation index (I_{geo}), potential ecological risk index (RI), sediment quality guidelines (SQGs), and risk assessment code (RAC), and finally, the sources of heavy metals are examined by principal component analysis and metallic ore geological tracing. However, the combination of statistical analysis and each index can offer a comprehensive understanding of the heavy metal risks of Qinjiang River sediments that can be employed to provide a scientific basis for environmental management and environmental legislation, including pollution control of Qinjiang River water bodies, substrate dredging, etc., so that relevant managers can make targeted adjustments to the regional industrial structure and formulate environmental protection methods that are more suitable to the Qinzhou City's development stage and the Qinjiang River's functional needs.

2. Materials and methods

2.1 Study area

The Qinjiang River is located in Qinzhou City, Guangxi Zhuang Autonomous Region, and belongs to the Pearl River system. It originates from Bainiuling at the eastern foot of Dongshan Mountain, Pingshan Town, Lingshan County, flows through more than half of Qinzhou City, and finally flows into the Maowei Sea from Shajing. With a total length of 195.26 km and a catchment area of 2391.34 km^2, it is the largest river flowing into the Maowei Sea area of Qinzhou Bay. It is a crucial water source for industrial and agricultural production and life in Qinzhou City. Meanwhile, the study area is situated in the subtropical monsoon climate zone, with abundant rainfall and usual floods and droughts.

2.2 Sample collection and pre-treatment

A total of 19 stations were chosen from the upstream to the Qinjiang estuary along the Qinjiang River Basin (marked as S1 to S19) (Fig. 1). The surface sediments (approximately 0–10 cm in depth) were obtained in December 2021 using a gravity sampler. All the surface sediments in contact with the sampler were cleaned with a plastic scraper to reduce the sediment samples' disturbance. Three parallel subsamples were obtained from each station. All samples were subsequently transported back to the laboratory in labeled polyethylene sealable bags and freeze-dried using a freeze drier (CHRIST Alpha2-4LSC basic). The frozen samples were then sequentially dried in natural air, dried at high temperature, ground, and passed through a 200-mesh nylon sieve to obtain the sample to be examined (Pacifico et al. 2007).

2.3 Physico-chemical analysis of sediments

Fresh samples were mixed at a water-to-soil ratio of 1:2.5 (Lu 1999) and centrifuged at 3500 rpm for 10 min; subsequently, the sediment pH and salinity were measured using a multiparameter analyzer (DZC-708); The total organic carbon (TOC) was determined by the loss-on-ignition (Ball 1964). The pretreated samples were roasted in a high-temperature muffle furnace (HT16/17, Nabertherm), and the content of organic matter (OM) in the samples was calculated according to the mass difference before and after, and the TOC content was finally converted using OM.

2.4 Microwave-assisted acid digestion and determination of metals

Aliquots of ~0.1 g of sediments were placed in digestion tanks containing a 5:4:2 mixture of HNO_3+ HF+ $HClO_4$. The samples were subsequently heated in a microwave digestion apparatus (CEM/MARS6) for the following cycle. At 1600 W of power, climb to 170°C for 30 min and maintain at that temperature for 20 min, climb to 210°C for 40 min and maintain at that temperature for 30 min (Peng & Wu 2017). Subsequently, insert the digested samples in an acid purifier at 150°C, and rush the acid to 1 ml. After cooling, the samples were diluted to 50 ml with ultrapure water and filtered through a 0.45 μm filter membrane, and finally, use a 50 ml centrifuge tube to perform the test.

The concentrations of Fe, Mn, Zn, Co, Ni, Cd, Cr, Cu, and Pb in samples extracted from sequential extraction and microwave digestion were measured using ICP-OES

(PEOptima8000, USA), and the quality control of the nine elements extracted was conducted to assure that the recoveries were in the range of 80%–120%.

2.5 Sequential extraction procedure（BCR）

Acid-soluble, reducible, oxidizable, and residual were extracted sequentially using the improved BCR-sequential extraction method (Rauret et al. 1999). Table 1 shows the extraction agent and target sediment fraction employed in each step. At the end of each extraction, the centrifuge tube was placed in a centrifuge at 4000 rpm for 10 min. The supernatant was collected, and the residue was cleaned with ultrapure water twice, transferred into a 50 mL volumetric flask, and fixed with 3% dilute nitric acid. After passing through a 45 µm filter membrane, the centrifuge tube was loaded with 50 mL for testing.

2.6 Contamination and risk assessment of heavy metals in sediments

2.6.1 Geo-accumulation index（I_{geo}）

The geo-accumulation index (I_{geo}) was first suggested by Muller, a scientist from the Sediment Research Institute of Heidelberg University in Germany, in 1969 (Müller 1981). It shows the pollution level through the heavy metal content in sediments, indicates the natural variation characteristics of the distribution of heavy metals, and determines the effect of human activities on the environment, which is a crucial parameter to differentiate the human activities' effect. This approach is a geochemical index for evaluating heavy metals in sediments, which is determined by the following equation:

$$I_{geo} = \log_2\left[C_n / k * B_n\right]$$

Where, C_n represents the determined concentration of heavy metal (mg/kg), k represents the correction coefficient considered due to the geological differences of rocks in various areas, which is generally 1.5, B_n denotes the heavy metal background concentration n (mg/kg). The background concentration of heavy metals in the soil employed in this study is as follows: Mn = 159.32, Zn = 48.25, Co = 14.60, Ni = 24.00, Cd = 0.07, Cr = 21.41, Cu = 11.31, and Pb = 20.43 (Jiang et al. 2020, Lin et al. 2021) (Fe rarely contaminates the environment, and therefore, there is no background value). According to the various I_{geo} values, the heavy metal pollution levels can be interpreted as follows: I_{geo}, no pollution; $0 < I_{geo} \leqslant 1$, low pollution; $1 < I_{geo} \leqslant 2$, near moderate pollution; $2 < I_{geo} \leqslant 3$, moderate pollution; $3 < I_{geo} \leqslant 4$, near high pollution; $4 < I_{geo} \leqslant 5$, high pollution; $5 < I_{geo} \leqslant 6$, very high pollution.

2.6.2 Potential ecological risk index

The potential ecological RI method is a set of approaches for evaluating heavy metal pollution and ecological damage developed by the famous Swedish scientist Hakanson based on sedimentology (Hakanson 1980). It covers several research fields combining biotoxicology, environmental chemistry, and ecology, the ecological risk of heavy metals on soil is comprehensively assessed, and the potential damage degree is quantitatively categorized (Table 4). The value of RI was computed using the following equations:

$$C_{\mathrm{f}}^{\mathrm{i}} = \frac{C^{\mathrm{i}}}{C_{\mathrm{n}}^{\mathrm{i}}},\ C_{\mathrm{d}} = \sum C_{\mathrm{f}}^{\mathrm{i}},\ E_r^i = T_r^i C_f^i,\ RI = \sum E_r^i$$

Where, $C_{\mathrm{f}}^{\mathrm{i}}$ represents the pollution coefficient of heavy metals i, C^{i} represents the determined concentration of heavy metals i (mg/kg), $C_{\mathrm{n}}^{\mathrm{i}}$ denotes the background values of heavy metals (mg/kg), C_{d} represents the sum of pollution coefficients of different heavy metals, E_r^i denotes the potential ecological risk factor, RI represents the potential ecological RIs; T_r^i denotes the toxicity coefficient of heavy metals, i denotes the toxicity level of heavy metals and the organisms' sensitivity to heavy metal pollution, and its values are Zn = 1, Cr = 2, Co = Ni = Cu = Pb = 5, and Cd = 30 (Islam et al. 2015). According to the determined level of toxicity of the heavy metals, it defined five categories of E_r^i ($E_r^i < 30$, low risk; $30 < E_r^i \le 60$, moderate risk; $60 < E_r^i \le 120$, considerate risk; $120 < E_r^i \le 240$, high risk; $E_r^i \ge 240$, very high risk) and four categories of RI ($RI < 60$, low risk; $60 < RI \le 120$, moderate risk; $120 < RI \le 240$, considerate risk; $RI > 240$, very high risk).

2.6.3 Sediment quality guidelines

The SQGs can be employed to evaluate the heavy metal pollution level in sediments. Theoretically, SQGs are derived from the accumulation of data sets of sediment chemistry and corresponding adverse biological impacts (Long et al. 1995, Macdonald et al. 1996), whereas the empirical assessment of SQGs is based on the total amount of heavy metals in sediments (Sarkar et al. 2017). There are two concentration thresholds for SQGs; one is unlikely to generate toxic reactions, and the other is likely to generate toxic reactions, and the pollutant concentrations between the two thresholds have significant uncertainty. To resolve this situation, it is crucial to conduct a site-specific analysis by observing the health and behavior of benthic organisms at the site. One frequently employed approach is to use the threshold effect level (TEL) and possible effect level (PEL) to compare with the heavy metal concentration to assess the degree of harmful impacts of sediment-related chemical states on benthic organisms (Long et al. 1998, MacDonald et al. 2000). These two levels defined three ranges of benthic hazards: no harm (＜TEL); may cause harm (＞TEL and ＜PEL); and harm (＞PEL).

Furthermore, as heavy metals always appear in complex mixtures in sediments, the heavy metals' ecological risk can also be further assessed by the PEL of heavy metals and the resulting mass fraction to yield the mean probable-effect-level quotient (mPEL-Q) (Gu 2018); the formula is as follows:

$$mPEL-Q = \sum_{i=1}^{n} \left(C_r^i / PEL_i \right) / n$$

where C_r^i represents the measured concentration of the heavy metal i, PEL_i represents the PEL for the heavy metal i, and n is the number of heavy metal species. The mPEL-Q indices can be grouped into the following four categories: mPEL-Q$\leqslant$0.1, low risk; 0.1$<$mPEL-Q$\leqslant$1, considerate risk; 1$<$mPEL-Q$\leqslant$5, high risk; mPEL-Q$>$5, very high risk.

2.6.4 Risk assessment code

The RAC was employed to evaluate the bioavailability and mobility of heavy metals in sediments (Perin et al. 1985), which is closely related to the concentration of heavy metals in the sequentially extracted acidic soluble. The RAC equation is as follows:

$$RAC = \frac{F1}{F1 + F2 + F3 + F4}$$

The RAC indices can be grouped into the following five categories: RAC＜1%, no risk; 1%＜RAC＜10%, low risk; 11%＜RAC＜30%, considerate risk; 31%＜RAC＜50%, high risk; RAC＞50%, very high risk.

3. Results and discussion

3.1 Total concentration and physicochemical properties of heavy metals in sediments of the Qinjiang River

Fig. 2 presents the pH values, salinity, and TOC concentration of sediments in the Qinjiang River. The pH of sediments in the Qinjiang River ranged from 6.119 to 7.147, with a mean value of 6.61 and a weak acidity generally; the variation range of salinity ranged from 0.01 to 0.24; the variation range of ω(TOC) ranged from 3.12% to 6.43%, with a mean value of 4.43%. When the point is closer to the Qinjiang River estuary, the pH tends to decrease as a whole, and salinity and TOC content tend to increase as a whole. Remarkably, pH has considerably lower values at S2, S12, S13, and S14, probably because the sampling area is close to the industrial park and the agricultural planting area. The sediment acidity was aggravated by the acidity of the water bodies caused by the sewage discharge and waste accumulation in the sampling area's vicinity. Furthermore, the stations with significant heavy metal concentrations also have high TOC, showing that the TOC content influences the heavy metals' enrichment.

Table 2 summarizes the characteristics of heavy metal concentrations in sediments in the Qinjiang River. Average total heavy metal concentrations (mg/kg) were discovered in the decreasing order as Fe (31401.95) > Mn (500.27) > Zn (112.49) > Cu (65.45) > Cr (29.78) > Pb (22.99) > Ni (17.82) > Co (9.05) > Cd (0.02); except for Co, Ni, and Cd, the concentrations of other heavy metals Mn, Zn, Cr, Cu, and Pb were higher than their background values of 3.14, 2.33, 1.39, 5.79, and 1.13 times, respectively. High concentrations of Mn, Cd, and Cu were discovered in S5, which is situated in the city center and has hospitals, markets, and Nixing pottery factories nearby. High concentrations of Fe and Pb were discovered in S12, which has several agricultural planting areas and industrial parks. A high concentration of Cr is distributed in the dock area. High concentrations of Zn, Co, and Ni were distributed in the aquaculture area (S18). Heavy metals in waste and polluted soil are readily leached into the near-source water via runoff, and heavy metals migrate through rivers and accumulate in sediments (Feng et al. 2019). Thus, these buildings may become the heavy metal pollution's primary source of sediments and must be addressed in the subsequent analysis.

The coefficient of variation (CV) can show the uniformity and degree of variation of heavy metals in soil stations. Generally, the larger the CV, the greater the spatial dispersion that may be influenced by human activities. Among them, the CV of Fe, Co, Ni, Cd, Cr, Cu, and Pb range from 7.64% to 26.49%, all of which are less than 30%, showing that the distribution of these seven heavy metals in the watershed is relatively stable and these heavy metals are primarily affected by natural factors. The coefficients of variation of Mn (53.55%) and Zn (37.02%) both exceeded 30%, depicting that the spatial dispersion of Mn and Zn was greater, and it is speculated that Mn and Zn are primarily affected by human activities.

3.2 Geochemical fractionations of heavy metals

Fig. 3 shows four geochemical fractions of nine heavy metals (Fe, Mn, Zn, Co, Ni, Cd, Cr, Cu, and Pb) in surface sediments at 19 stations in the Qinjiang River extracted by the improved BCR-sequential extraction method. Therefore, different proportions of geochemical fractions of heavy metals can be grouped into the following three categories: the first category is Mn, which is primarily found in the acid-soluble fraction (F1) and accounts for 38.92%, depicting that Mn has high bioavailability and is easily released under acidic conditions; the second category is Zn, which is mainly found in the oxidizable fraction (F3) and accounts for 54.50%. Such heavy metals primarily occur in the form of iron and manganese oxides and organically bound states, which migrate with the change of redox potential, resulting in secondary pollution of water; the third category is Fe, Co, Ni, Cd, Cr, Cu, and Pb, and these seven heavy metals are primarily discovered in the residual fraction (F4). The average proportion of F4 is 78.13%, 57.39%, 56.60%, 55.36%, 55.31%, 73.74%, and 62.88%, respectively, and some investigations have depicted (Teasdale et al. 2003) that the residual fraction of heavy metals was almost not being used by organisms. This can have a specified effect on organisms only by converting them into a soluble fraction by chemical reactions. Thus, these seven heavy metals are relatively stable in the Qinjiang River sediments and cannot easily cause pollution to the ecological environment.

3.3 Pollution and risk assessment

3.1.1 Geo-accumulation index（Igeo）

Fig. 4 shows the I_{geo} values of the eight heavy metals. All heavy metals are in the decreasing order of Cu(1.94) > Mn(0.87) > Zn(0.18) > Cr(−0.17) > Pb(−0.44) > Ni (−1.02) > Co (−1.31) > Cd (−2.40). The negative I_{geo} values for Co, Ni, and Cd at all stations show a no pollution level; although the mean value of Cr and Pb is negative, there are still individual stations, which belong to low pollution. The mean value of Mn and Zn is between 0 and 1 (low pollution). However, at individual stations, Mn reaches 1 to 2 (moderate pollution) and 2 to 3 (moderate pollution). The mean I_{geo} value of Cu is much higher than other heavy metals, i.e., close to 2 to 3 (moderate pollution), showing that Cu is the most polluted heavy metal in the study area.

3.1.2 Potential ecological risk index

Fig. 5 shows the values of potential ecological risk factors (E_r^i). The E_r^i of all heavy metals were discovered in the decreasing order as Cu(28.95) > Cd(8.78) > Pb(5.63) > Ni(3.71) > Co(3.10) > Mn(3.14) > Cr (2.78) > Zn (2.33), and all heavy metals depicted low risk. The E_r^i values of Cu, Mn, Co, Ni, Cr, Cu, and Pb were consistent with the results generated by the I_{geo} values. However, Cd and Zn show a different result, which is probably because the E_r^i primarily shows the heavy metal toxicity level and the organisms' sensitivity to heavy metal pollution. When this approach is employed for risk assessment of heavy metals, the heavy metals' toxicity coefficient has a significant influence on the results.

Fig. 6 shows the values of the potential ecological risk index (RI). There are six stations in the Qinjiang River whose RI values are greater than 60 (medium ecological risk), and the RI values of these stations were discovered in the decreasing order as S5(67.05) > S4 (65.09) > S9 (64.47) > S8 (61.91) > S12 (61.44). Consistent with the results of the total concentration of heavy metals, higher RI values were discovered at S5 and S18, showing a higher ecological risk at these two stations. According to the field investigation, it is speculated that the pollution of S5 is due to intensive human activities and industrial pollution, including hospitals, markets, and Nixing pottery factories, whereas the pollution at S18 arises from the adjacent aquaculture area.

3.1.3 Sediment quality guidelines（SQGs）

Considering the limitations of I_{geo} and RI approach, another approach was used according to SQGs, based on the heavy metals' total concentration. In this study, a set of SQGs rules about the TEL and PEL was employed to determine the ecotoxicological implications of seven heavy metals (Zn, Ni, Cd, Cr, Cu, and Pb) in the Qinjiang River.

Table 3 shows the results. The mean concentrations of Cd and Cr at all stations are less than TEL, depicting that neither Cd nor Cr will harm benthic organisms; Zn, Ni, and Pb have 19%, 21%, and 85% of the stations whose concentrations are lower than TEL, respectively, and 81%, 79%, and 15% of which are between TEL and PEL, showing that Zn and Ni may cause harmful impacts to benthic organisms occasionally at some stations; Mn was less than the PEL at most stations (94%); however, it was the only heavy metal in the study that exceeded the PEL at one station (S5). Thus, Mn contamination at station S5 must be addressed. The mean concentrations of Cu at all stations were between TEL and PEL, indicating that Cu may be harmful to benthic organisms.

Additionally, the mPEL-Q values of each station were computed to further investigate its risk level, and **Error! Reference source not found.** shows the results. The mPEL-Q varied within the range 0.16–0.26, between 0.1 and 1, which belonged to the considerate risk. Among them, the mPEL-Q's relatively higher value appeared at S5 and S18, which is consistent with the results of the potential ecological risk assessment in the previous article. Thus, it can be determined that the high-value areas of heavy metals in the sampling area are situated at stations S5 and S18.

3.1.4 Risk assessment code

In the study by Singh et al. (Singh et al. 2005), it was depicted that among numerous heavy metal geochemical fractions, changes in acid-soluble caused by human activities influence the bioavailability or mobility of heavy metals in sediment. Thus, when the percentage of acid-soluble in geochemical fractions is higher, the higher the migration capacity of heavy metals in sediments, the higher the bioavailability, and the higher the level of potential ecological risk. Fig. 7 shows the RAC evaluation results of heavy metals in sediments in the Qinjiang River. The mean RAC value of each heavy metal decreased in the order of Mn (38.92%) > Zn (13.43%) > Cr (12.68%) > Cu (7.70%) > Fe (1.48%) > Cd (0.75%) > Pb (0.69%) > Co (0.62%) > Ni (0.49%). According to RAC, Mn appeared to pose a high risk, Zn and Cr were grouped as medium risk, Fe and Cu were grouped as low risk, and Co, Ni, Cd, and Pb were grouped as no risk. However, it should be noted that the results of Cu are different from those of I_{geo} and RI, probably because the RAC approach is based on the heavy metals' geochemical fractions and their proportion to characterize the risk level and does not consider the total concentration of heavy metals, and the bioavailability expressed in the geochemical fractions is unequal to biological toxicity considered by I_{geo} and RI. In this study, the total concentration of Cu is higher than the background values; however, Cu's presence in the sediment is primarily in the residual fractions, which are more stable and less likely to be released in the sediment and cause harm to the ecological environment.

3.4 Source analysis

Based on the risk assessment of different heavy metals in Qinjiang River sediments, personal correlation analysis, principal component analysis, and cluster analysis were conducted on nine heavy metals in the study area using SPSS25.0 to further investigate the possible sources of heavy metals in Qinjiang River sediments.

3.4.1 Principal component analysis

Based on personal correlation analysis, the sources of heavy metals were further examined by principal component analysis (PCA) of nine heavy metals. The matrix Kaiser–Meyer–Olkin test value was 0.598, indicating that the data were suitable for PCA (Fig. 8). It was observed that the eigenvalues of principal components 1 and 2 are 3.948 and 1.784, respectively, and the variance contribution rates are 43.869 and 19.819, which can better demonstrate the data situation. In the first component (PC1), Fe, Cr, Pb, and Cd demonstrated highly positive loadings, indicating that Fe, Cr, Pb, and Cd may have the same source; in second component (PC2), Zn, Co, and Ni have considerably positive loadings, showing that Zn, Co, and Ni may have the same source; but Cu and Mn have highly negative loadings, also depicting that Cu and Mn may share the same source.

Table 4 shows the correlations between the nine investigated heavy metals, pH, salinity, and TOC. It was observed that there is a considerable negative correlation between pH and salinity and TOC, depicting that salinity and TOC decrease with the increase of pH; Fe, Zn, Ni, Cr, Pb, and TOC manifested substantial positive correlations, depicting that there is a close relationship between the TOC in the soil and total heavy metal concentrations; it was depicted in a study (Schiff & Weisberg 1999) that Fe is less influenced by human interference because of its high concentration, and therefore, it can be employed as a characterization of human and natural factors. In this study, Fe has a considerable positive correlation with Cr and Pb ($p < 0.01$), and therefore, both Cr and Pb are derived from natural factors. Simultaneously, Cd has a substantial positive correlation with Fe, Cr, and Pb ($p < 0.05$) and indicates low risk in both the I_{geo} and RI, indicating that Cd also belongs to natural factors; Cu and Mn were considerably positively correlated ($p < 0.01$).

I_{geo} indicated that Mn and Zn were higher than soil background values and had evident characteristics of foreign pollution. PCA and correlation analysis indicated that the two groups of heavy gold denoted by Mn and Zn belong to various sources; the contents of Mn, Cu, and Cd are related to pH, while Zn, Fe, Pb, Co, Ni, and Cr are related to TOC and salinity. Combined with the analysis of heavy metal components, the composition of Mn includes the Carbonate-Bound Fraction and the Fe-Mn-Oxides-Bound Fraction, and the Zn component is the Organio-Bound Fraction. Qinzhou Port is also the largest distribution center of manganese ore in China (Fan & Yang 1999). The Upper Devonian Liujiang Formation is the primary manganous-bearing strata in the Qinzhou area. Manganese is present in the form of manganese carbonate minerals, like rhodochrosite, calcite, manganese siderite, and manganese dolomite, while manganese in sediments or weathering crust is in the form of secondary oxides, accompanied by Cu, Cd, and other elements (Lang et al. 2007). Zinc deposits in the Qinjiang River Basin occur in the Indo-Hercynian granitic rock mass in Pubei County, Qinzhou City. The zinc deposits are primarily sphalerite, which has a symbiotic relationship with Pb to generate lead-zinc deposits and form an organic combination with OM and pyrite after weathering and leaching (Carter et al. 2001).

In conclusion, heavy metal pollution in surface sediments was primarily from manganese ore and zinc ore mining in the Qinjiang River, because manganese ore is more than zinc ore and manganese pollution level is higher than zinc (Xia et al. 2012). Manganese carbonate and its weathered secondary manganese oxide are typically

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associated with a significant amount of residual copper and Cd, and their concentrations are usually influenced by pH; that is, higher pH is suitable for the deposition and enrichment of these heavy metals, but lower pH may form acidic dissolved states and migrate to estuarine shelf. Lead-zinc ore and its weathering products generate organic compounds with residual Fe, Co, Cr, and Ni, and their content is related to salinity. The possible reason is that the weathering process of lead-zinc ore causes the conversion of low sulfur into sulfate radical and the release of associated metal elements.

4. Conclusions

The total concentration, contamination condition in the environment, and sources in sediments of the Qinjiang River were evaluated using the improved BCR-sequential extraction method, and the results are as follows.

(1) In this study, the total concentrations of heavy metals were discovered in the decreasing order as Fe > Mn > Zn > Cu > Cr > Pb > Ni > Co > Cd, and they are all significantly lower than the background values, except Mn, Zn, Cr, Cu, and Pb. Mn was primarily the acid-soluble, showing that it was readily released under acidic conditions and caused environmental damage; Zn had a high content in the reducible, which had a significant potential ecological risk and was prone to secondary pollution; however, Fe, Co, Ni, Cd, Cr, Cu, and Pb were primarily in the residual, which is more stable in the sediment and difficult to release.

(2) According to the results obtained by I_{geo}, RI, SQGs, and RAC, Cu, Mn, and Zn cause pollution and have certain ecological risks in the Qinjiang River. However, Cu, which exists primarily in the form of residue, poses less ecological risk than Mn and Zn, showing that Cu is not the primary pollutant in the Qinjiang River; Fe, Co, Ni, Cd, Cr, and Pb are unharmful to the environment because of their low content in sediments and natural source heavy metals, but attention must be paid toward their prevention and control.

(3) I_{geo}, BCR, and PCA indicate that heavy metal pollution in surface sediments is primarily due to manganese and zinc ore mining in the Qinjiang River. Manganese carbonate and its weathered secondary manganese oxide are typically associated with a significant amount of residual copper and Cd, and a higher pH is suitable for the deposition and enrichment of these heavy metals. Lead-zinc ore and its weathering products generate organic compounds with residual Fe, Co, Cr, and Ni, and their content is related to salinity.

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Figure Captions

Fig. 1. location of the study area and sample sites

Fig. 2. Physicochemical characteristics of sediment at the different stations.

Fig. 3. Percentage distribution of heavy metals in four geochemical fractions at 19 stations.

Fig. 4. Geo-accumulation index (I_{geo}) values of heavy metals in surface sediments from the Qinjiang river.

Fig. 5. Values of potential ecological risk factor (E_r^i) of heavy metals in the sediments of Qinjiang River.

Fig. 6. Values of potential ecological risk index (RI) at different stations.

Fig. 7. Risk assessment code(RAC) values of heavy metals in surface sediments from the Qinjiang river.

Fig. 8. PCA loadings of components 1 and 2 for the nine heavy metals in surface sediments from the Qinjiang river.

Fig. 9. Geological map (1:200000) and mineral distribution around the Qinjiang river. (Survey 2013)

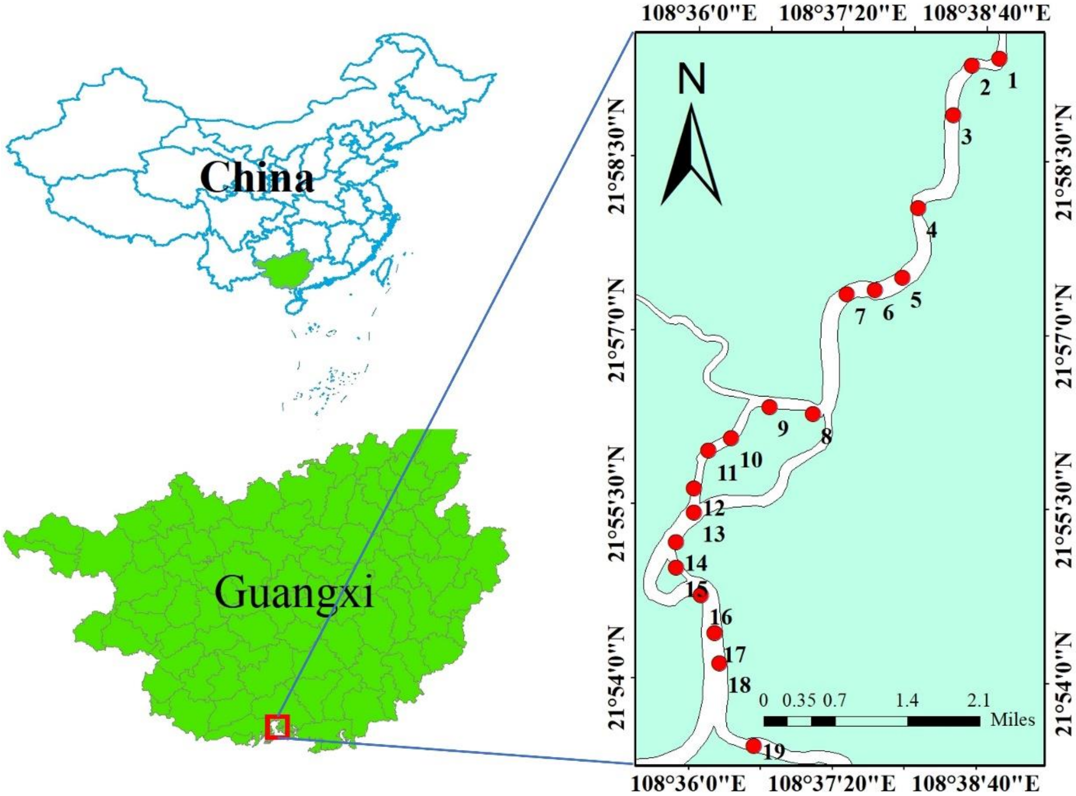

Fig. 10. location of the study area and sample sites

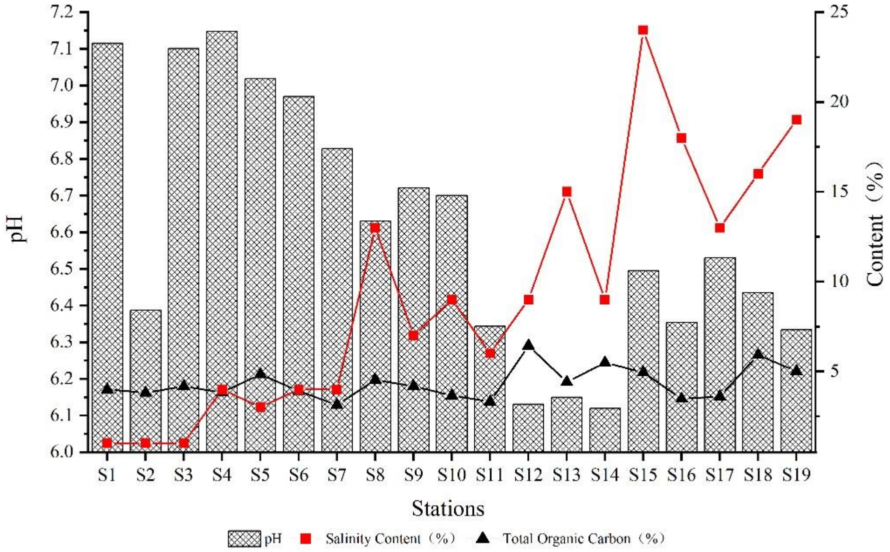

Fig. 11. Physicochemical characteristics of sediment at the different stations.

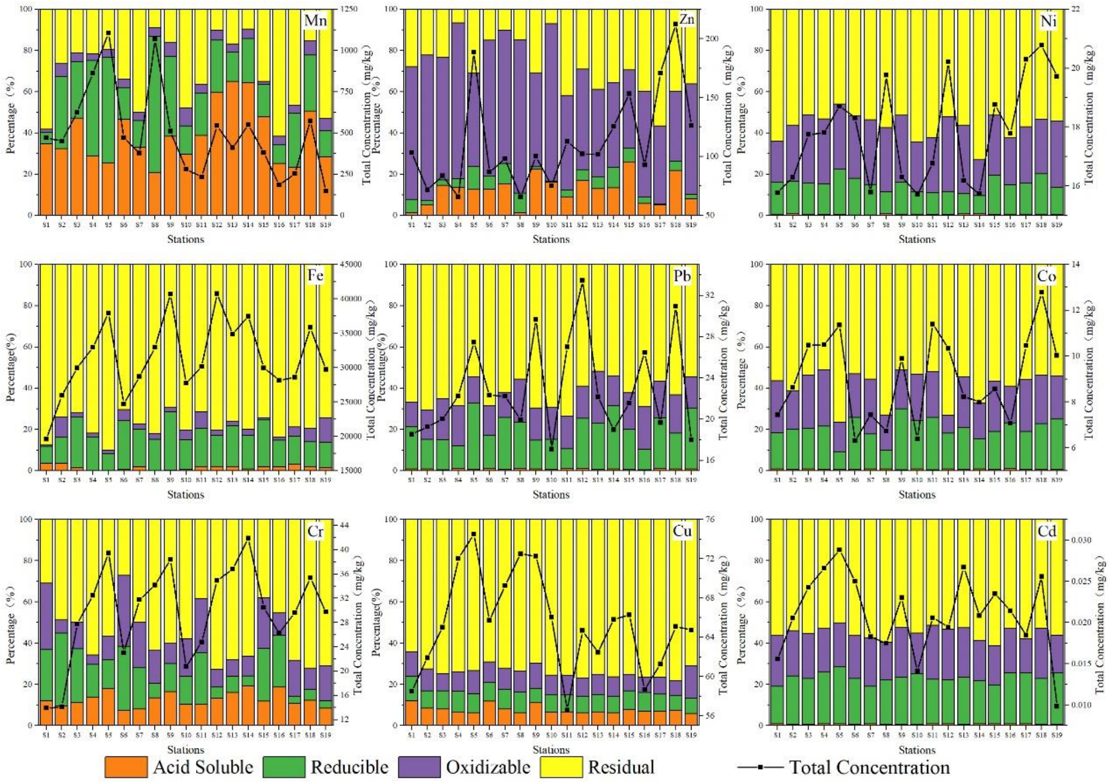

Fig. 12. Percentage distribution of heavy metals in four geochemical fractions at 19 stations.

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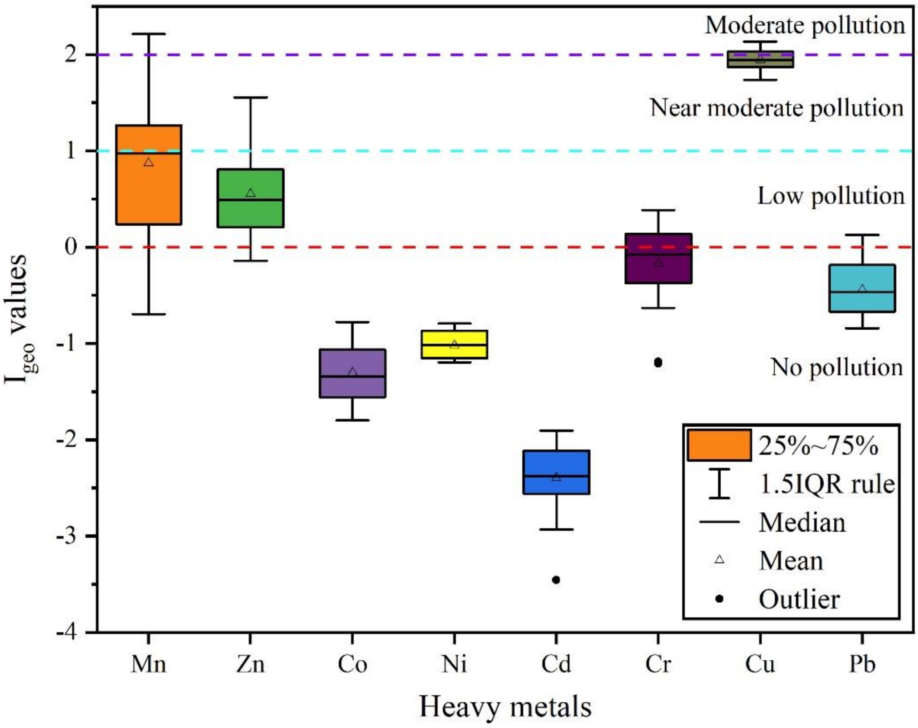

Fig. 13. Geo-accumulation index (I_{geo}) values of heavy metals in surface sediments from the Qinjiang river.

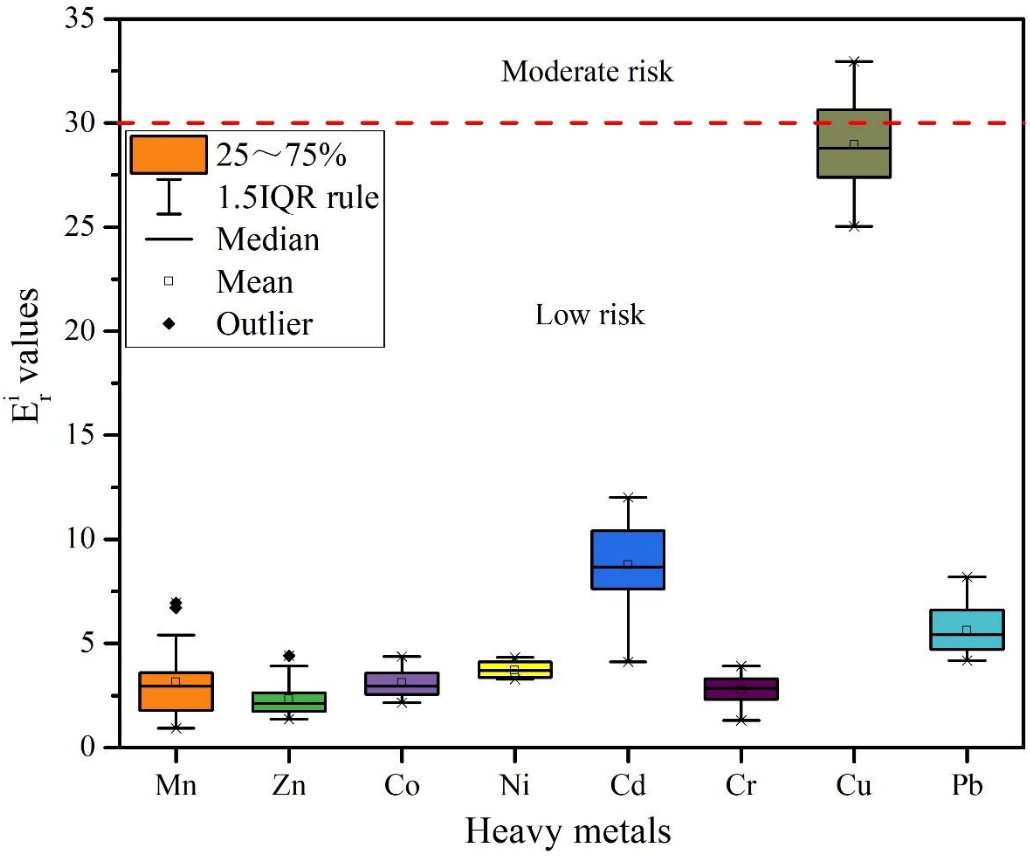

Fig. 14. Values of potential ecological risk factor (E_r^i) of heavy metals in the sediments of Qinjiang River.

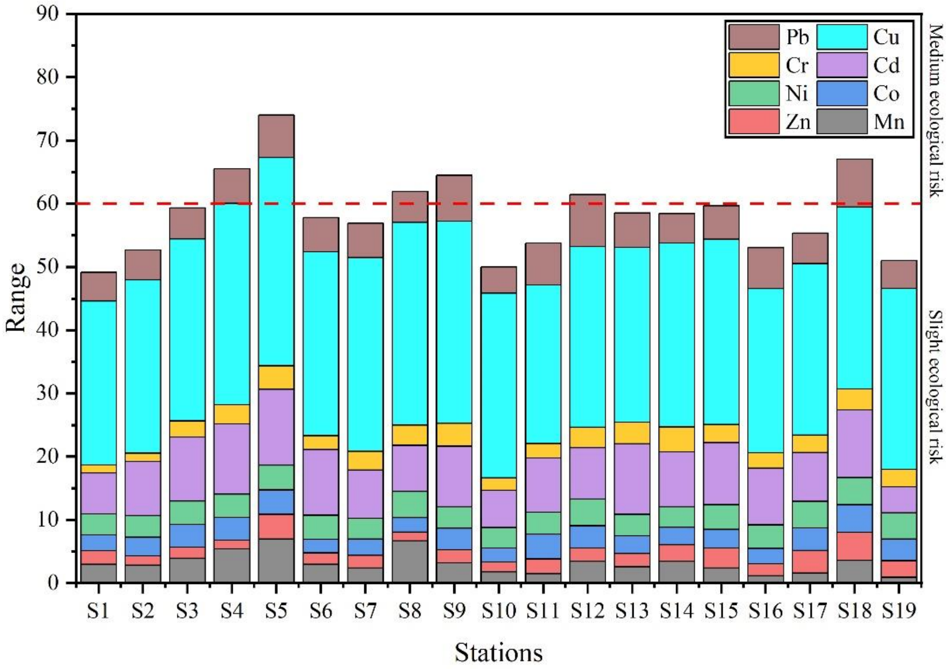

Fig. 15. Values of potential ecological risk index (RI) at different stations.

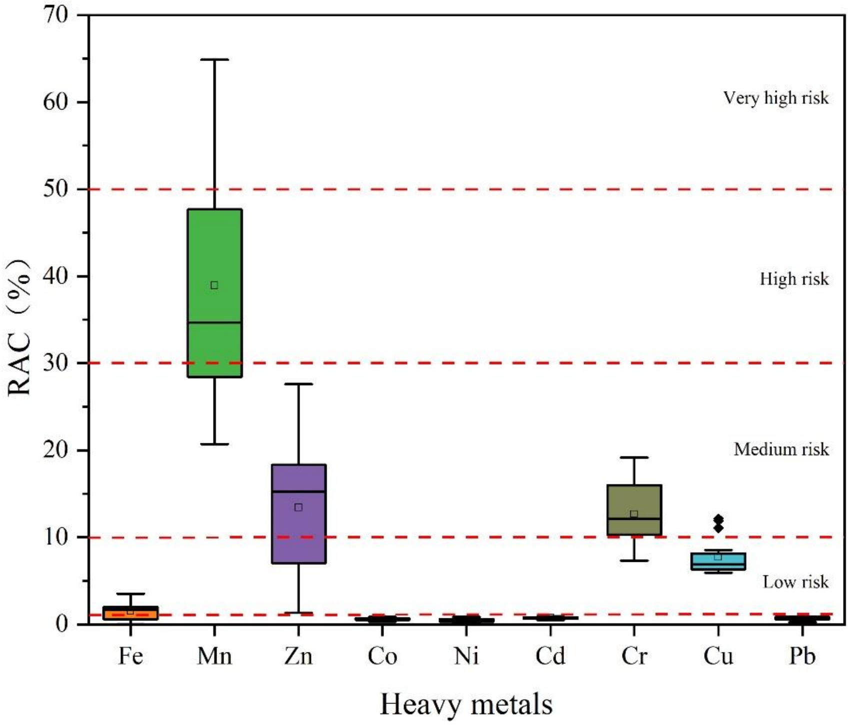

Fig. 16. Risk assessment code(RAC) values of heavy metals in surface sediments from the Qinjiang river.

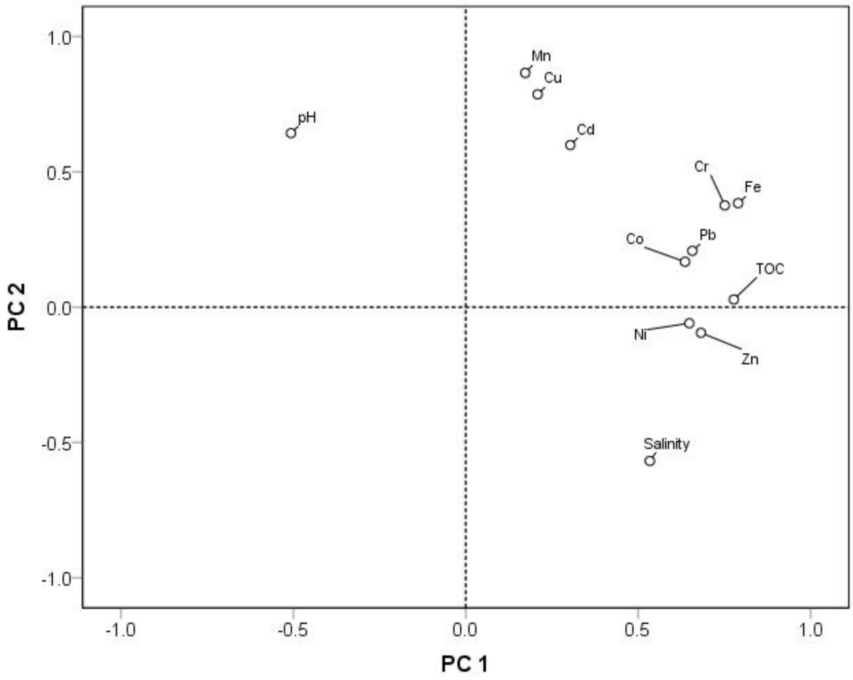

Fig. 17. PCA loadings of components 1 and 2 for the nine heavy metals in surface sediments from the Qinjiang river.

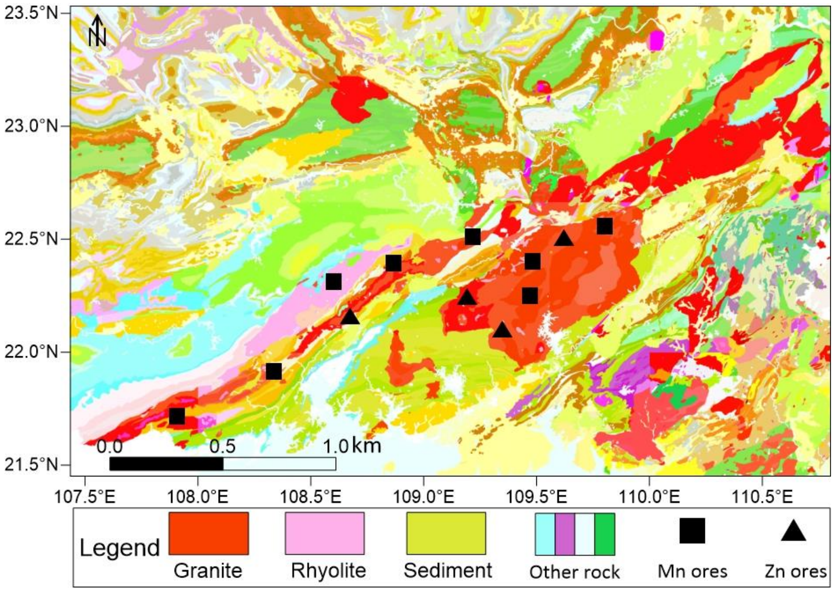

Fig. 18. Geological map (1:200000) and mineral distribution around the Qinjiang river. (Survey 2013)

Table 1 Improved BCR-sequential extraction procedure

Step	Extracting agent	Extraction process
F1（Acid Soluble）	20mL, 0.11mol/L CH_3COOH	Shaking at 220rpm at 22±5℃ for 16h
F2（Reducible）	20ml,0.5mol/L NH_2OH-HCl（PH=1.5）	Shaking at 220rpm at 22±5℃ for 16h
F3（Oxidizable）	10ml,30% H_2O_2；25ml,1.0mol/L CH_3COONH_4（PH=2）	Heated 85℃ for 1h. Shaking at 220rpm at 22±5℃ for 16h
F4（Residual）	2.5 ml HNO_3，2.0 ml HF，1.0 ml $HClO_4$	Microwave digestion

Table 2 Values of maximum, minimum, median, average, background (in mg/kg) and coefficient of variation (CV%) for total concentration of heavy metals in the surface sediments from the Qinjiang River.

Elements	Maximum	Minimum	Median	Average	Background	CV
Fe	40776.19	19576.20	29971.10	31401.95	—	17.66%
Mn	1106.67	147.57	469.66	500.27	159.32	53.55%
Zn	212.44	65.67	101.74	112.49	48.25	37.02%
Co	12.78	6.30	8.63	9.05	14.60	21.08%
Ni	20.79	15.72	17.80	17.82	24.00	9.87%
Cd	0.03	0.01	0.02	0.02	0.07	22.75%
Cr	41.92	13.90	30.49	29.78	21.41	26.49%
Cu	74.52	56.60	65.10	65.45	11.31	7.64%
Pb	33.47	17.08	22.16	22.99	20.43	20.74%

Table 3

Percentage of heavy metals in each category associated with biological risks.

Heavy metals		Fe	Mn	Zn	Co	Ni	Cd	Cr	Cu	Pb
TEL (Gu 2018, Xu et al. 2017)		—	460	124	—	15.9	0.68	52.3	18.7	30.2
PEL (Gu 2018, Xu et al. 2017)		—	1100	271	—	42.8	4.21	160.4	108.2	112.2
The comparison with TEL and PEL		%of samples in each guideline								
I	<TEL	—	47	19	—	21	100	100	0	85
II	>TEL and <PEL	—	47	81	—	79	0	0	100	15
III	>PEL	—	6	0	—	0	0	0	0	0

Table 4

Pearson correlation matrix for heavy metals concentration in surface sediments from the Qinjiang river.

Elements	Fe	Mn	Zn	Co	Ni	Cd	Cr	Cu	Pb	PH	Salinity	TOC
Fe	1.000											
Mn	.405*	1.000										
Zn	0.279	0.012	1.000									
Co	.481*	0.157	.601**	1.000								
Ni	0.254	0.202	.491*	.459*	1.000							
Cd	.390*	.479*	0.234	0.331	0.045	1.000						
Cr	.879**	.405*	.389*	0.353	0.280	.393*	1.000					
Cu	.519*	.729**	0.007	0.053	0.141	0.290	.576**	1.000				
Pb	.631**	0.158	0.339	.532**	0.342	.457*	.425*	0.106	1.000			
PH	-0.350	.433*	-0.170	-0.055	-0.126	0.200	-0.251	.397*	-0.200	1.000		
Salinity	0.169	-0.341	0.369	-0.005	.461*	-0.155	0.305	-0.117	0.056	-.581**	1.000	
TOC	.620**	0.294	.446*	0.370	.511*	0.116	.526*	0.219	.402*	-.394*	0.334	1.000

Note: *Correlation is significant at the 0.05 level. **Correlation is significant at the 0.01 level.