


Heavy metals and metalloids in the surface sediments of the Xiangjiang River, Hunan, China: distribution, contamination, and ecological risk assessment

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Abstract Here, we aim to determine the distribution, ecological risk and sources of heavy metals and metalloids in the surface sediments of the Xiangjiang River, Hunan Province, China. Sixty-four surface sediment samples were collected in 16 sites of the Xiangjiang River, and the concentrations of ten heavy metals and metalloids (Mn, Zn, Cr, V, Pb, Cu, As, Ni, Co, and Cd) in the sediment samples were investigated using an inductively coupled plasma mass spectrometer (ICP-MS) and an atomic fluorescence spectrophotometer (AFS), respectively. The results showed that the mean concentrations of the ten heavy metals and metalloids in the sediment samples followed the order $Mn > Zn > Cr > V > Pb > Cu > As \approx Ni > Co > Cd$. The geoaccumulation index (I_{geo}), enrichment factor (EF), modified degree of contamination (mC_d), and potential ecological risk index (RI) revealed that Cd, followed by Pb, Zn, and Cu, caused severely contaminated and posed very highly potential ecological risk in the Xiangjiang River, especially in Shuikoushan of Hengyang, Xiawan of Zhuzhou, and Yijiawan of Xiangtan. The Pearson's correlation coefficient

(PCC) analysis, principal component analysis (PCA), and hierarchical cluster analysis (HCA) indicated that the ten heavy metals and metalloids in the sampling sediments of the Xiangjiang River were classified into three groups: (1) Cd, Pb, Zn, and Cu which possibly originated from Shuikoushan, Xiawan, and Yijiawan clustering Pb–Zn mining and smelting industries; (2) Co, V, Ni, Cr, and Al from natural resources; and (3) Mn and As. Therefore, our results suggest that anthropogenic activities, especially mining and smelting, have caused severe contamination of Cd, Pb, Zn, and Cu and posed very high potential ecological risk in the Xiangjiang River.

Keywords Sediments · Heavy metals and metalloids · Xiangjiang River · Contamination indices · Ecological risk

Introduction

River sediments are the basic and integral components of fluvial ecosystems, not only providing nutrients for benthic organisms, but also serving as sinks and sources for pollutants, such as heavy metals and metalloids (Akçay et al. 2003; Jiang et al. 2013; Pejman et al. 2015). Globally, the river aquatic ecosystems have been continuously receiving significant amounts of anthropogenic heavy metals and metalloids from industrial, agricultural, and urban disposals for several decades (Feng et al. 2004; Jamshidi-Zanjani and Saeedi 2013; Yang et al. 2009b). Once entering in the rivers, heavy metals and metalloids, regardless of whether they are dissolved or not, are rapidly diluted and transported with hydrologic gradients for hundreds of kilometers and consequently deposited and accumulated in the sediments (Audry et al. 2004; Tam and Wong 2000). However, contaminated sediments are the potential nonpoint sources of heavy metals and metalloids,

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which may directly pollute overlying waters and pose environmental risk to the fluvial ecosystems, through altering their pH and redox potential, sediment perturbations, and migration of the contaminated benthic biota (Zhao et al. 2015b; Zhao et al. 2014). Therefore, it is a suitable tool to assess the negative influences of heavy metals and metalloids on a fluvial ecosystem by monitoring their contamination status and ecological risk in the sediments (Ciszewski et al. 2012; Heim and Schwarzbauer 2013; Li et al. 2013; Nazeer et al. 2014; Wang et al. 2012).

In the past decades, a series of geochemical and statistical indices has been developed to assess the pollution status and ecological risk of heavy metals and metalloids in the sediments (Dung et al. 2013; Jamshidi-Zanjani and Saeedi 2013; Li et al. 2013; Mamat et al. 2016; Yi et al. 2016). So far, geoaccumulation index (I_{geo}), enrichment factor (EF), potential ecological risk index (RI), modified degree of contamination (mC_d), contamination factor (CF), pollution load index (PLI), sediment quality guidelines (SQG), ratio pollution index (RPI), and risk assessment code (RAC) have been extensively employed to assess the contamination and ecological risk of heavy metals and metalloids in the sediments of marine and fluvial ecosystems (Bednarova et al. 2013; Cheng et al. 2015; Dung et al. 2013; Ghrefat et al. 2011; Hu et al. 2013; Jamshidi-Zanjani and Saeedi 2013; Jiang et al. 2013; Mamat et al. 2016; Nazeer et al. 2014; Pejman et al. 2015; Wang et al. 2015; Yi et al. 2016; Zhao et al. 2015a; Zhu et al. 2013b). The I_{geo} is a widely utilized classical geochemical criterion to evaluate the pollution degree of heavy metals and metalloids in sediments (Cheng et al. 2015; Mamat et al. 2016; Yi et al. 2016). The EF is commonly used to assess the contamination status by evaluating the natural or anthropogenic sources of metals in sediments (Bednarova et al. 2013; Mamat et al. 2016; Yi et al. 2016). However, they only focus on individual pollutant, while multi-metal contamination in sediments is common. The mC_d produces an overall average value for a range of pollutants to comprehensively assess the extent of contamination in sediments (Cheng et al. 2015). Unlike I_{geo} , EF, and mC_d , the RI is a combination ecological risk assessment of toxicity, migration, and transformation of heavy metals and metalloids in sediments (Jamshidi-Zanjani and Saeedi 2013; Pejman et al. 2015; Yi et al. 2016). The bivariate and multivariate statistical methods, Pearson's correlation coefficient (PCC) analysis, principal component analysis (PCA), factor analysis (FA), and hierarchical cluster analysis (HCA) are also increasingly applied to identify the origin and evaluate the contaminated status of heavy metals and metalloids in rivers and sediments (Jiang et al. 2013; Liu et al. 2003; Pejman et al. 2015; Peluso et al. 2013; Varol 2011; Zhao et al. 2015a; Zhu et al. 2013b).

The Xiangjiang River is the main river in Hunan province, China, with major cities, industry, agriculture, and population of the province, as well as with one of the Chinese top 5 lead

(Pb) and zinc (Zn) ore zones in the basin. The river was historically and dramatically polluted by heavy metals and metalloids, due to mining and smelting nonferrous metals for hundreds of years in the basin. Heavy metal and metalloid pollutants in the river have been a critical environmental concern in Hunan province in the last decades and caused increasing attention on the contamination status and ecological risk (Han et al. 2014; Jiang et al. 2013; Mao et al. 2013; Zhu et al. 2013a). However, the study to systematically and comprehensively investigate the contamination status and the ecological risk of heavy metal contamination in the whole Xiangjiang River is limited. Here, we aim to (1) determine the distribution of heavy metals and metalloids (Pb, Zn, copper (Cu), chromium (Cr), cadmium (Cd), nickel (Ni), arsenic (As), cobalt (Co), manganese (Mn), and vanadium (V)) in the surface sediments of the whole Xiangjiang River; (2) assess the contamination status of the heavy metal and metalloid pollutants from different angles with geoaccumulation index (I_{geo}), enrichment factor (EF), and modified degree of contamination (mC_d) and the ecological risk by potential ecological risk index (RI); and (3) identify the potential sources of the heavy metals and metalloids by Pearson's correlation coefficient (PCC) analysis, principal component analysis (PCA), and hierarchical cluster analysis (HCA).

Materials and methods

Study area

The Xiangjiang River, one of the major tributaries of the Yangtze River, is the chief river in Hunan province, China, deriving from the Haiyang Mountain, Lingui county, Guangxi province (Fig. 1). Flowing entirely in Hunan province with typical subtropical monsoon climate, the river rises in southwestern Yongzhou and meanders slowly northward for 856 km to the Dongting Lake, successively passing through Yongzhou, Hengyang, Zhuzhou, Xiangtan, Changsha, and Yueyang districts. The basin totally covers 44.66 % (94,660 km²) of the Hunan province's area and holds the major cities, industry, agriculture, and population of the province. The basin, deposits abundant nonferrous metal mineral resources, such as Pb, Zn, Cu, and Mn, and as a result, mining and smelting nonferrous metals for hundreds of years have caused severe heavy metal and metalloid contamination in the fluvial ecosystem, especially in the Hengyang and Zhuzhou sections. To systematically and comprehensively investigate the contamination status and ecological risk of the heavy metal and metalloid pollutants in the Xiangjiang River, we, therefore, selected different sampling locations: the origin of the river in Hunan, areas clustering mining and smelting factories, cities, dams, and the mouth of the river (Fig. 1).

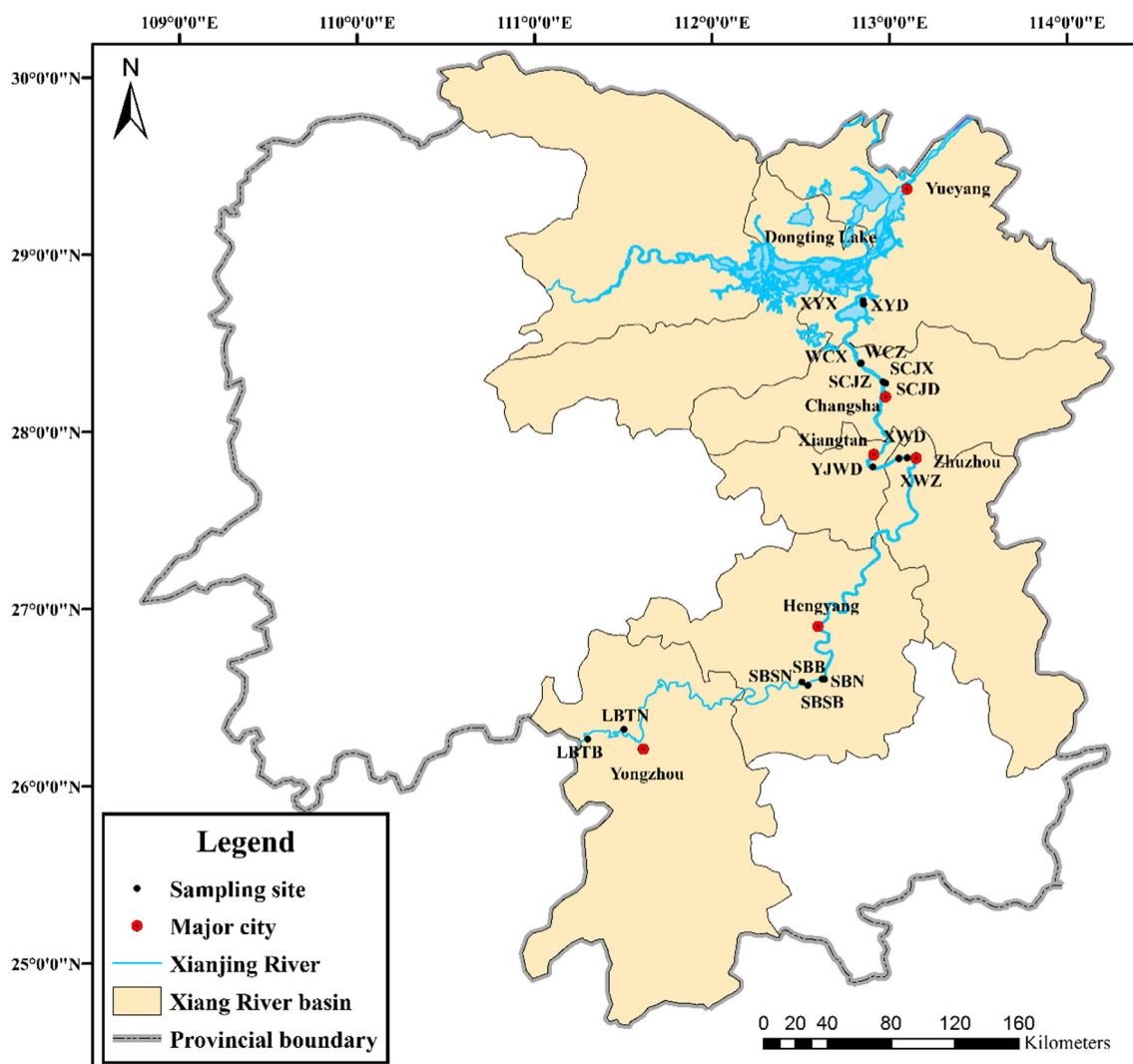


Fig. 1 Map displaying the study area and sampling sites in the Xiangjiang River

Sediment sampling

The sampling sites are located in both sides of the Xiangjiang River. Here, the 16 sampling sites were selected in seven sections, as follows: The sites of Lvbutou, Yongzhou, are located in the origin of the Xiangjiang River of Hunan province (LBTB and LBTN). The sites of Shuikoushan, Hengyang (SBSB, SBSN, SBB, and SBN); Xiawan, Zhuzhou (XWB and XWZ); and Yijiawan, Xiangtan (YJWD) were in the areas clustering mining and smelting factories. The sites in Sanchaji (SCJD, SCJZ, and SCJX) were in Changsha city, and the site in Yijiawan (YJWD) was also in Xiangtan city. The sites in Wangcheng, Changsha (WCX and WCZ), were located before a dam. The sites in Xiangying, Yueyang (XYX and XYD), are the mouth of the Xiangjiang River to the Dongting Lake. As the sampling strategy, four surface sediment (depth:0–15 cm) samples

for each sampling site were collected by a grab sampler (ZYC-200B, Hangzhou Yijie Technology Co. Ltd., Hangzhou, China) and stored in clean plastic bags prior to shipping to the laboratories.

Heavy metal and metalloid analyses

The heavy metals and metalloids in the sediment samples were determined following the protocols previously published (Liao et al. 2014; Lin et al. 2013; Wang et al. 2013). Briefly, the sediment samples were desiccated at 60 °C for 14 days, followed by desiccation at 110 °C for 2 days. The dry samples were grounded, homogenized, and sieved with 100-mesh nylon sieves (150 μm) for chemical analyses. Of well-prepared sediment sample, 40.00 mg was completely digested by 1 ml HNO₃ plus 3 ml HF at 130 °C for 72 h sealed in a Teflon shaker. Next, 0.5 ml of HClO₄ was added after cooling of the

treated samples and heated with cap opened to 120 °C for 12 h until the white smoke was gone. Then, the residue was dissolved with 1 ml HClO₄ and 1 ml ddH₂O in a sealed shaker for 12 h. Finally, the solution was diluted to 40 ml by ddH₂O in a Teflon bottle at room temperature for the next step. The concretions of Al, Pb, Zn, Cu, Cr, Cd, Ni, Co, Mn, and V were simultaneously determined with an inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500 series, USA). In addition, 300.00 mg of the identical sediment sample was digested with 10 ml aqua regia at 95 °C for 2 h, followed by adding 5 ml HCl, 5 ml thiocarbamide, and aqua regia to 50 ml. The concentration of As was determined by an atomic fluorescence spectrophotometer (AFS-810, Beijing Titan Instrument Corp., Beijing, China). The average value of each metal in the four samples of a sampling site was considered as the concentrations of the metal for the site. In order to guarantee the quality of the analysis, laboratory quality assurance and control methods were implemented, including the standard operating procedures, standard calibration, reagent blank analysis, and repeated analysis. Blanks and China Stream Sediment Reference Materials (GBW07309 (GSD-9) and GBW07311 (GSD-11)) were performed for quality assurance and quality control, and recoveries of the standard reference metals were 92–104 %. In addition, each analysis was performed in triplicate and the SD was within ±5 % of the mean value.

Evaluating contamination status of heavy metals and metalloids in the surface sediments

Geoaccumulation index

Since formulated by Müller in 1969, the geoaccumulation index (*I_{geo}*), a classical assessment model, was widely utilized to quantify the heavy metal and metalloid contamination in soils and sediments by the following formula (Audry et al. 2004; Cheng et al. 2015; Dung et al. 2013; Ghrefat et al. 2011; Jiang et al. 2013; Liu et al. 2009; Müller 1969; Shi and Wang 2013):

$$I_{geo} = \log_2 \left(\frac{Me_{\text{sediment}}}{1.5Me_{\text{baseline}}} \right) \tag{1}$$

where *Me_{sediment}* is the concentration of the examined heavy metal and metalloid, and *Me_{baseline}* is the geochemical background value (average shale) or the preindustrial level for the identical element. The constant value 1.5 is the background matrix correction factor due to lithogenic effects. Here, the background concentration of heavy metals and metalloids in the soils of Hunan province in 1980s was denoted as *Me_{baseline}* (Table 5) (China National Environmental Monitoring Center

1990). The classification of *I_{geo}* shown in Table 1 was proposed by Müller (Jiang et al. 2013).

Enrichment factor

The enrichment factor (EF) was also utilized to assess the degree of heavy metal and metalloid contamination in sediments (Acevedo-Figueroa et al. 2006; Audry et al. 2004; Bednarova et al. 2013; Dung et al. 2013; Ghrefat et al. 2011; Jiang et al. 2013; Zhu et al. 2013b). The formula was as follows:

$$EF = \frac{(Me/Al)_{\text{sample}}}{(Me/Al)_{\text{baseline}}} \tag{2}$$

where (Me/Al)_{sample} is the concentration ratio of a heavy metal or a metalloid to Al in the tested sample and (Me/Al)_{baseline} is the ratio of the same element to Al in the geochemical background. Aluminum (Al) generally serves as the normalizing element to calculate the EFs of heavy metal and metalloid. The background values of the soils in Hunan province mentioned previously were used as the reference values. The categories of EF are summarized in Table 2 (Acevedo-Figueroa et al. 2006).

Modified degree of contamination

The modified degree of contamination (*mC_d*) developed by Abraham and Parker (Abraham and Parker 2008; Cheng et al. 2015) was applied to evaluate the comprehensive contamination of multiple heavy metals and metalloids in each sediment sample. The equations to calculate *mC_d* are as follows:

$$C_f^i = \frac{Me_{\text{sample}}^i}{Me_{\text{baseline}}^i} \tag{3}$$

$$mC_d = \frac{\sum_{i=1}^n C_f^i}{n} \tag{4}$$

Table 1 Standard of contamination levels by geoaccumulation index (*I_{geo}*)

<i>I_{geo}</i> value	Class	Quality of sediment
<0	0	Unpolluted
0–1	1	From unpolluted to moderately polluted
1–2	2	Moderately polluted
2–3	3	From moderately to strongly polluted
3–4	4	Strongly polluted
4–5	5	From strongly to extremely polluted
>5	6	Extremely polluted

Source: Jiang et al. (2013)

Table 2 Contamination categories based on enrichment factor (EF)

EF value	Class	Enrichment category
<1	0	No enrichment
1–3	1	Minor enrichment
3–5	2	Moderate enrichment
5–10	3	Moderately severe enrichment
10–25	4	Severe enrichment
25–50	5	Very severe enrichment
>50	6	Extremely severe enrichment

Source: Acevedo-Figueroa et al. (2006)

where C_f^i is the contamination factor of the element i and Me_{sample}^i and Me_{baseline}^i are the concentrations of the element i in the sample and in the background, respectively; n is the number of the analyzed elements. The mC_d is categorized in Table 3 (Abraham and Parker 2008).

Assessing potential ecological risk of heavy metals and metalloids in the surface sediments

The potential ecological risk index (RI) proposed by Hakanson (1980) was utilized to quantitatively assess the ecological risk degree of heavy metals and metalloids in aquatic sediments (Jamshidi-Zanjani and Saeedi 2013; Pejman et al. 2015; Zhu et al. 2013b). RI is defined as follows:

$$E_r^i = T_r^i \times C_f^i = T_r^i \frac{Me_{\text{sample}}^i}{Me_{\text{baseline}}^i} \quad (5)$$

$$RI = \sum E_r^i, \quad (6)$$

where E_r^i is the potential ecological risk factor of the heavy metal or metalloid i , T_r^i is the toxic response factor of the element i , Me_{sample}^i is the concentration of the element i in the examined sediments, and Me_{baseline}^i is the background concentration of the element i . The T_r^i s for Pb, Zn, Cu, Cr, Cd, Ni, As, Co, Mn, and V are 5, 1, 5, 2, 30, 5, 10, 5, 1, and 2,

Table 3 Classifications for modified degree of contamination (mC_d)

mC_d value	Class	Contamination situation
$mC_d < 1.5$	0	Nil to very low degree of contamination
$1.5 \leq mC_d < 2$	1	Low degree of contamination
$2 \leq mC_d < 4$	2	Moderate degree of contamination
$4 \leq mC_d < 8$	3	High degree of contamination
$8 \leq mC_d < 16$	4	Very high degree of contamination
$16 \leq mC_d < 32$	5	Extremely high degree of contamination
$32 \leq mC_d$	6	Ultra high degree of contamination

Source: Abraham and Parker (2008)

respectively (Cao et al. 2009; Jamshidi-Zanjani and Saeedi 2013). The evaluated criteria of RI are classified in Table 4.

Statistical analysis

Principle component analysis (PCA) was performed as the previous protocols (Jiang et al. 2013; Peluso et al. 2013; Zhao et al. 2015a; Zhu et al. 2013b). Briefly, the Kaiser-Meyer-Olkin (KMO) and Bartlett sphericity tests were performed to examine the validity of PCA and the covariance matrix was built based on the measured values of all heavy metals and metalloids in sediment samples followed by eigenvalue decomposition. According to the values and contribution rates of the eigenvalues (>1), the principle components were selected and the principle component values of the samples were calculated by the measured values of the elements with varimax rotation. Hierarchical cluster analysis (HCA) was generated on the standardized data sets (Z-cores) by the Euclidean distance method and the Ward method, and as a result, the dendrogram visually demonstrated the cluster relationship between the ten heavy metals and metalloids (Jiang et al. 2013; Tang et al. 2014; Zhu et al. 2013b). The relationship among metals and metalloids was also analyzed by Pearson's correlation matrix to verify the results by multivariate analysis. The PCA, HCA, and Pearson's correlation analyses were processed by SPSS 18 for Windows (SPSS, Inc., USA).

Results and discussion

Contamination distribution of the ten heavy metals and metalloids in the surface sediments of the Xiangjiang River

The concentrations of metals and metalloids in the surface sediments of the Xiangjiang River are summarized in Table 5. Generally, the concentrations of Pb, Zn, Cu, Cr, Cd, Ni, As, Co, Mn, and V ranged from 24.45 to 672.3, 30.7–1009.65, 24.55–250.05, 67.9–170, 4.25–31.2, 15.95–187.2, 13.55–122.1, 7.85–53.9, 748.05–3412, and 43.95–210.6 mg/kg dry weight, respectively. The mean concentrations of these metals in the sediment samples followed the order $Mn > Zn > Cr > V > Pb > Cu > As \approx Ni > Co > Cd$ (Table 5). Geographically, the highest concentrations of Pb, Zn, Cu, Cd, and As were clustered in the sites SBN of Shuikoushan, Hengyang, and XWD and XWZ of Xiawan, Zhuzhou, which were consistent with those of the major Pb and Zn mining and smelting factories located in the two areas. Similar results were shown in the previous researches on the Xiangjiang River (Han et al. 2014; Jiang et al. 2013; Mao et al. 2013; Zhu et al. 2013a). Compared with other rivers and lakes in China, the concentrations of the ten heavy metals and metalloids in the surface sediments of the Xiangjiang River caused

Table 4 The potential ecological risk criteria for heavy metal and metalloid contamination

E_r^i value	Class	Level of single metal ecological risk	RI value	Class	Level of comprehensive potential ecological risk
$E_r^i < 40$	1	Low risk	$RI < 150$	1	Low risk
$40 \leq E_r^i < 80$	2	Moderate risk	$150 \leq RI < 300$	2	Moderate risk
$80 \leq E_r^i < 160$	3	Considerable risk	$300 \leq RI < 600$	3	Considerable risk
$160 \leq E_r^i < 320$	4	High risk	$600 \leq RI$	4	Very high risk
$320 \leq E_r^i$	5	Very high risk			

Source: Zhu et al. (2013b)

serious concern and indicated that, therefore, anthropogenic activities possibly had caused heavy metal and metalloid contamination in the river (Fu et al. 2014; Hu et al. 2013; Li et al. 2013; Lin et al. 2013; Liu et al. 2003; Tang et al. 2014; Wang et al. 2015; Zhao et al. 2015a; Zhu et al. 2013b). Interestingly, the highest concentrations of Cr, Ni, Co, and V were in the site LBTB (Lvbutou in Yongzhou), while the concentrations of heavy metals and metalloids in the site LBTN were much lower than in the site LBTB. It is possibly that these heavy metals were from the mining and smelting activities in Guangxi province and were transported with hydrologic gradients (Audry et al. 2004; Liu et al. 2014; Tam and Wong 2000).

Contamination status

Geoaccumulation index

According to the standard of geoaccumulation index (I_{geo}) in Table 1, Cd had caused severe pollution (class 6) in all sampling sites, while Pb, Zn, Cu, As, and Mn had caused moderate contamination (classes 2 and 3) (Fig. 2a). The contamination status of the ten heavy metals and metalloids were dramatically variant in different geographical sampling sites. Strong contaminations of Pb, Zn, Cu, and As were clustered in the sampling sites SBN, XWD, XWZ, and YJWD in which several large-scaled Pb–Zn mining and smelting factories were distributed, while Mn was moderately polluted in the river randomly (Fig. 2a). Moreover, the contaminations of the heavy metals and metalloids were more severe in urban and industry areas (SBB, SBN, XWD, XWZ, YJWD, SCJD, SCJZ, and SCJX) than in agriculture areas (LBTB, LBTN, XYX, and XYD) (Fig. 2a). All sampling sites were rarely polluted by Cr, Ni, Co, and V ($I_{geo} < 1$).

Enrichment factor

To explore the potential sources of heavy metals and metalloids (anthropogenic and/or natural) in the surface

sediments of the Xiangjiang River, enrichment factor (EF) was applied by calculating the degree of metal contamination compared to the background (Acevedo-Figueroa et al. 2006; Bednarova et al. 2013; Dung et al. 2013; Jiang et al. 2013). Al was selected as the conservative reference element because it is rich in the earth’s crust and assumed inert to anthropogenic activities (Acevedo-Figueroa et al. 2006; Wang et al. 2015). Generally, an EF value between 0.5 and 1.5 suggests that the given heavy metal or metalloid may be entirely from crustal materials or natural weathering processes. However, it is considered as a significant portion from anthropogenic sources when the EF value is greater than 1.5 (Zhang and Liu 2002; Zhang et al. 2009). The EF values of Cd (range 39.08–247.87; average 119.42) were highest in this study, indicating an extremely severe enrichment mainly from anthropogenic mining and smelting activities (Table 2; Fig. 2b). The following metals and metalloids were Pb (range 1.91–19.35), Zn (range 0.54–8.75), Cu (range 1.70–8.02), and As (range 0–8.27), and the mean values of them were 7.96, 5.17, 4.09, and 3.85, respectively, which suggested that they also originated from anthropogenic sources in most samples, especially in Shuikoushan of Hengyang, Xiawan of Zhuzhou, and Yijiawan of Xiangtan (Fig. 2b). Only V (range 0.95–2.45; average 1.22) was minor enriched, indicating that they are entirely from crustal materials or natural weathering processes (Table 2; Fig. 2b).

Modified degree of contamination

Different from I_{geo} and EF revealing the contamination status of single element, the modified degree of contamination (mC_d) modified from the degree of contamination (C_d) was applied to calculate the average contamination value of all heavy metals and metalloids in sediment samples (Abraham and Parker 2008). The contamination status shown by mC_d in the Xiangjiang River was similar with the results by I_{geo} and EF mentioned previously: the whole river was, at least, contaminated in high degree (class 3, Table 3) by all heavy metals and metalloids

Table 5 Concentration of heavy metals and metalloids in the surface sediments of the Xiangjiang River (mg/kg)

Sites	Pb	Zn	Cu	Cr	Cd	Ni	As	Co	Mn	V	Al (%)
LBTB	83.1 ± 12.33	113 ± 8.70	71.2 ± 18.15	170 ± 47.37	9.1 ± 8.25	187.2 ± 29.23	86.1 ± 29.59	53.9 ± 14.60	1650 ± 195.74	210.6 ± 58.54	6.98 ± 0.67
LBTN	104.05 ± 60.80	30.7 ± 17.92	31.95 ± 20.61	88.5 ± 24.73	4.55 ± 2.41	27.55 ± 9.17	17.7 ± 9.59	7.85 ± 3.98	1777.5 ± 433.02	60.1 ± 18.19	5.13 ± 0.68
SBSB	104.05 ± 23.47	197.3 ± 54.09	24.55 ± 13.38	72.55 ± 42.91	11.6 ± 4.13	15.95 ± 2.06	13.55 ± 5.70	ND	987.85 ± 166.27	43.95 ± 15.51	3.20 ± 0.54
SBSN	212.65 ± 25.58	417.55 ± 99.51	32.25 ± 17.05	67.9 ± 27.74	7.85 ± 3.08	33.9 ± 15.01	17.85 ± 7.82	12.95 ± 6.83	748.05 ± 222.42	76.35 ± 27.89	5.94 ± 1.69
SBB	25.45 ± 19.48	195.9 ± 61.30	34.25 ± 9.65	82.25 ± 17.20	14.1 ± 2.00	25.4 ± 9.69	14.7 ± 2.72	ND	1071.5 ± 242.52	54.55 ± 20.15	3.86 ± 0.93
SBN	380.2 ± 71.28	709.55 ± 129.70	205.9 ± 50.39	84.45 ± 13.88	16.55 ± 3.25	49.8 ± 12.95	122.1 ± 48.47	16.15 ± 2.64	2481 ± 214.02	121.85 ± 17.89	8.04 ± 0.88
XWD	672.3 ± 128.66	862.45 ± 89.47	250.05 ± 32.31	162.15 ± 32.50	15.35 ± 1.25	89.2 ± 12.41	99.95 ± 19.40	31.75 ± 12.92	1201.5 ± 295.96	159.6 ± 35.38	10.00 ± 1.45
XWZ	594.35 ± 66.13	1009.65 ± 189.44	221.1 ± 32.65	129.3 ± 31.37	31.2 ± 13.02	77.25 ± 29.37	53.2 ± 9.71	40.25 ± 12.56	1361.5 ± 302.51	160.6 ± 31.71	10.45 ± 2.00
YJWD	633.325 ± 86.84	936.05 ± 168.52	235.575 ± 87.97	145.725 ± 72.79	23.275 ± 3.89	83.225 ± 13.62	76.575 ± 17.37	22.55 ± 5.37	1281.5 ± 137.10	160.1 ± 49.46	10.22 ± 1.35
SCJD	48.95 ± 20.18	154.9 ± 45.83	58.85 ± 18.19	131.8 ± 33.52	4.25 ± 1.73	38.3 ± 13.52	25.2 ± 12.68	18.1 ± 4.22	1034.5 ± 179.80	104.3 ± 16.14	7.38 ± 1.34
SCJZ	83.75 ± 36.78	541.95 ± 108.23	99.35 ± 20.61	134.95 ± 39.51	18.05 ± 10.81	60.5 ± 11.88	25.65 ± 9.14	26.3 ± 7.15	2994.5 ± 390.52	118 ± 12.78	8.95 ± 0.93
SCJX	76.85 ± 24.26	441 ± 76.52	66.65 ± 21.58	161.9 ± 46.07	16.7 ± 5.32	47.05 ± 28.46	49.9 ± 12.33	23.5 ± 6.80	2103.5 ± 705.51	112.05 ± 20.88	8.36 ± 1.44
WCX	125.075 ± 25.60	374.15 ± 52.53	79.6 ± 30.21	114.65 ± 24.74	12.95 ± 4.21	50.3 ± 8.69	48.05 ± 8.99	20.15 ± 5.17	2624.75 ± 359.06	118.975 ± 32.20	8.73 ± 0.84
WCZ	126.35 ± 36.28	484.8 ± 56.19	84.5 ± 26.52	141.45 ± 38.89	16.3 ± 5.00	50.1 ± 15.13	118.05 ± 16.73	18.45 ± 3.19	3412 ± 411.24	151.4 ± 33.26	8.91 ± 1.19
XYX	98.85 ± 26.90	331.1 ± 34.60	58.2 ± 19.08	132.05 ± 52.03	9.2 ± 2.37	40.8 ± 9.25	ND	12.25 ± 3.56	2240.5 ± 252.02	107.3 ± 25.99	8.83 ± 1.12
XYD	69.3 ± 12.54	293 ± 129.97	67.85 ± 14.87	107.35 ± 38.54	7.8 ± 1.75	37.75 ± 11.25	ND	20.55 ± 4.89	1912.5 ± 435.39	111.5 ± 31.93	9.36 ± 1.55
Min	25.45	30.7	24.55	67.9	4.25	15.95	13.55	7.85	748.05	43.95	3.20
Max	672.3	1009.65	250.05	170	31.2	187.2	122.1	53.9	3412	210.6	10.45
Mean	214.913	443.316	101.364	120.436	13.677	57.142	54.898	23.193	1805.166	116.952	7.77
BV	29.7	94.4	27.3	71.4	0.126	31.9	15.7	14.6	549	105.4	8.55

ND not detected, BV background values (China National Environmental Monitoring Center 1990)

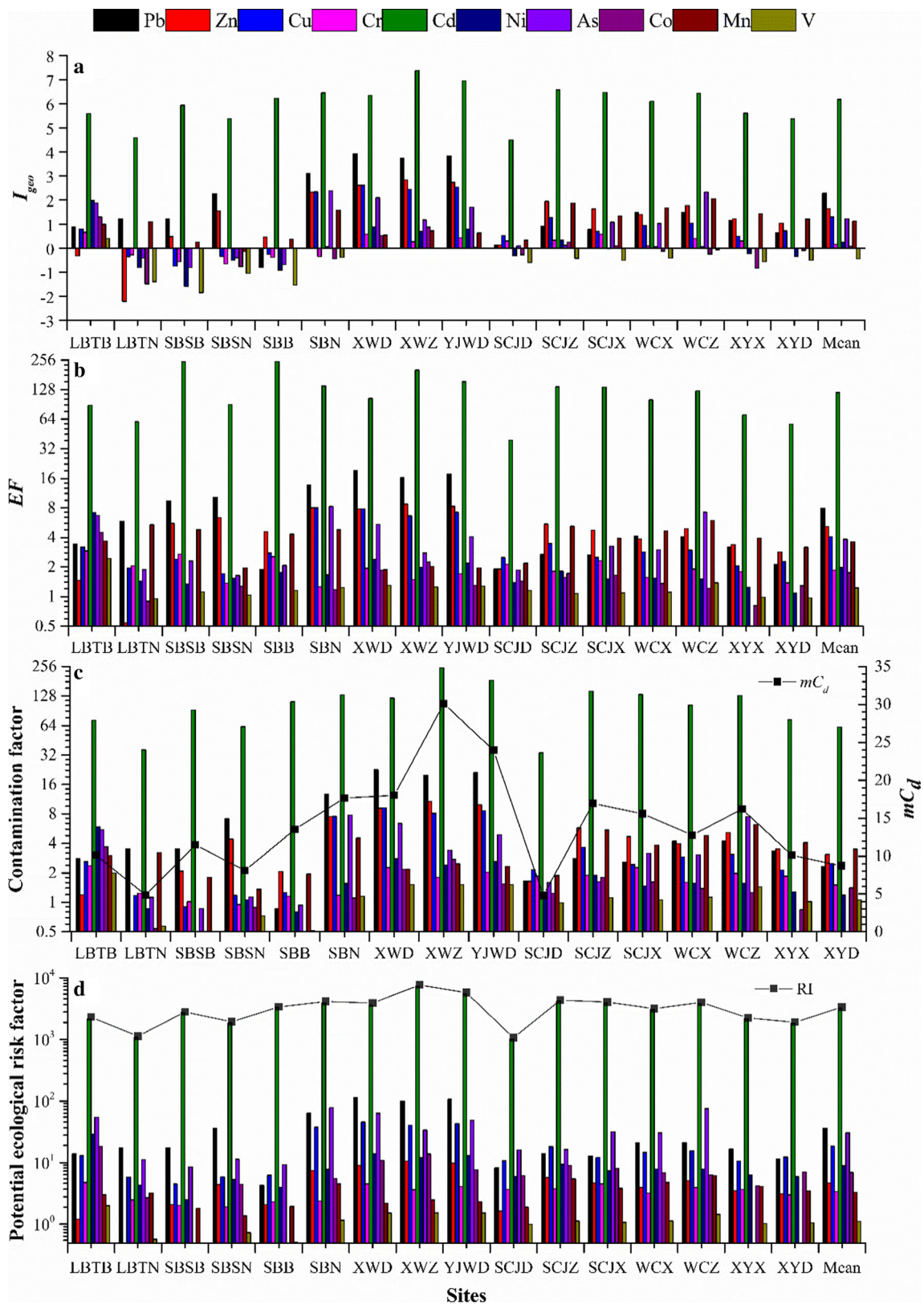


Fig. 2 The geoaccumulation indexes (I_{geo}) (a) enrichment factors (EF) (b), modified degree of contamination (mC_d) (c), and potential ecological risk index (RI) (d) of heavy metals and metalloids (Pb, Zn, Cu, Cr, Cd, Ni, As, Co, Mn, and V) in the surface sediments of 16 sampling sites in the Xiangjiang River

and very high degree of contamination (class 4, Table 3) clustered in Shuikoushan (SBN), Xiawan (XWD and XWZ), and Yijiawan (YJWD) (Fig. 2c).

Potential ecological risk

The potential ecological risk index (RI) is a comprehensive assessment of toxicity, migration, and transformation of heavy metals and metalloids in sediments (Hakanson 1980; Zhu et al. 2013b). As shown in Fig. 2d, according to the values of the average of potential ecological risk factor (E_r^i), the ecological risk of the ten heavy metals and metalloids ranked as the following order: Cd (3256.32) \gg Pb (36.18) > As (30.59) > Cu (18.56) > Ni (8.96) > Co (6.95) > Zn (4.70) > Cr (3.37) > Mn (3.29) > V (1.11) in all sampling sites of the Xiangjiang River. The results indicated that Cd caused most severe potential ecological risk in the river, although its concentration was the lowest in all heavy metals and metalloids (Fig. 2d). Conversely, Mn induced low potential ecological risk (class 1, Table 4) in the Xiangjiang River, while its concentration was the highest in all the ten heavy metals and metalloids in the sampling sediments (Fig. 2d). Geographically, Pb induced a considerable potential ecological risk (class 3, Table 4) in the sampling sites XWD, XWZ, and YJWD, and Pb, Cu, and As induced a moderate risk (class 2, Table 4) in SBN, XWD, XWZ and YJWD, although Pb, Cu, and As were of low risk in other sites (Fig. 2d). The results of RI indicated that there was a very high potential risk in all sampling sites of the Xiangjiang River due to extremely severe potential ecological risk of Cd and the trend in the whole river was similar with the I_{geo} , EF, and mC_d . The results also suggested that long-term mining and smelting nonferrous metals are tightly associated with severe heavy metal and metalloid contamination and posed incredibly severe

potential ecological risk in the Xiangjiang River (Mao et al. 2013; Zhu et al. 2013a).

Based on the results of total concentration, I_{geo} , EF, mC_d , and RI described previously, three groups of the ten metals and metalloids could be distinguished with different contamination behaviors: (1) Cd had a unique behavior that it caused severe contamination and posed a very high ecological risk in the whole river, but its concentration in all samples was the lowest among the metals. It is possibly that Cd is more sensitive to anthropogenic activities, as well as that Cd has a major chemical form more easily to dissolve and transport in sediments (Yang et al. 2009a). (2) Pb, Zn, Cu, and As showed highly variable distributions related to local pollution where major Zn–Pb mining and smelting factories are located. Such contamination distribution is also consistent with the pollutants emitted from the current techniques of Zn–Pb mining and smelting in China (Qi et al. 2016). (3) Cr, Ni, Co, Mn, and V showed homogeneous distributions among all sampling sites with low contamination level.

Potential resources of the ten heavy metals and metalloids

To further investigate the relationship and identify the potential sources of heavy metals and metalloids in sediments, bivariate and multivariate statistical analyses, such as Pearson's correlation coefficient (PCC) analysis, principle component analysis (PCA), and hierarchical cluster analysis (HCA), were frequently applied (Jiang et al. 2013; Peluso et al. 2013; Tang et al. 2014; Zhao et al. 2015a; Zhu et al. 2013b). In all of the metal pairs, the relationship was positive at 99 % confidence level, except the pair Pb–Mn in the Pearson's correlation matrix (Table 6). As shown in Table 6, Pb, Zn, Cu, and Cd had a significant positive correlation (>0.66) with each other ($P < 0.01$), while Ni, Co, and V composed another group (>0.866), indicating that two groups possibly originated from

Table 6 Pearson's correlation matrix for the heavy metal and metalloid concentrations in the surface sediments of the Xiangjiang River

	Pb	Zn	Cu	Cr	Cd	Ni	As	Co	Mn	V
Pb	1	<i>0.890**</i>	<i>0.930**</i>	0.238	<i>0.661**</i>	0.287	0.520	<i>0.355**</i>	<i>-0.247**</i>	0.469
Zn		1	<i>0.912**</i>	0.300	<i>0.849**</i>	0.189	<i>0.521**</i>	0.362	<i>0.049**</i>	0.493
Cu			1	0.388	<i>0.714**</i>	0.372	<i>0.647**</i>	<i>0.467**</i>	0.002	0.611
Cr				1	0.283	<i>0.676**</i>	0.425	0.747	0.263	0.802
Cd					1	0.202	<i>0.421**</i>	<i>0.348**</i>	<i>0.135**</i>	0.425
Ni						1	0.507	0.892	0.010	<i>0.866**</i>
As							1	<i>0.459*</i>	<i>0.331**</i>	0.675
Co								1	0.111	<i>0.908**</i>
Mn									1	0.253
V										1

Italic represents statistically significant correlation

***Significant correlation at the 0.01 level (two tailed); significant correlation at the 0.05 level (two tailed)

Table 7 Eigenvalues, variables and rotation of principal component analysis (PCA)

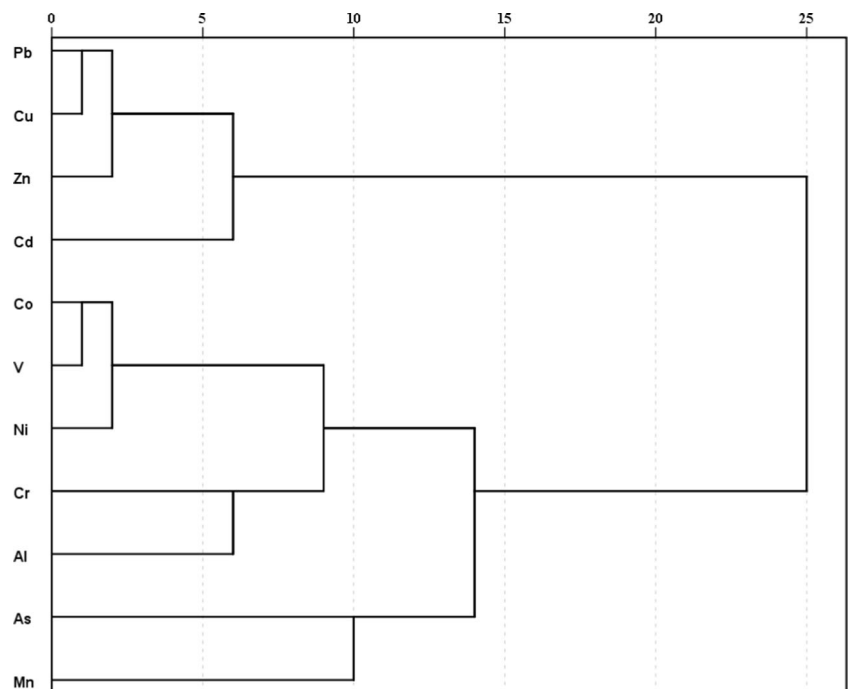
Initial eigenvalue				Component matrix				Rotation component matrix			
Component	Total	Of variance (%)	Cumulative (%)	Variables	PC1	PC2	PC3	Variables	PC1	PC2	PC3
1	5.463	54.625	54.625	Pb	0.761	-0.567	-0.219	Pb	0.918	0.195	-0.261
2	2.101	21.006	75.632	Zn	0.792	-0.563	0.102	Zn	0.966	0.137	0.052
3	1.168	11.678	87.309	Cu	0.867	-0.427	-0.013	Cu	0.915	0.311	-0.017
4	0.570	5.696	93.005	Cr	0.696	0.508	0.013	Cr	0.147	0.822	0.215
5	0.322	3.220	96.225	Cd	0.701	-0.459	0.202	Cd	0.838	0.120	0.164
6	0.206	2.063	98.288	Ni	0.710	0.562	-0.317	Ni	0.091	0.951	-0.088
7	0.073	0.727	99.015	As	0.749	0.036	0.292	As	0.537	0.467	0.376
8	0.045	0.449	99.464	Co	0.793	0.481	-0.214	Co	0.215	0.927	0.001
9	0.032	0.321	99.785	Mn	0.157	0.322	0.914	Mn	-0.029	0.096	0.977
10	0.022	0.215	100.000	V	0.899	0.398	-0.024	V	0.366	0.896	0.176

Extraction method: principal component analysis; rotation method: varimax with Kaiser normalization and rotation converged in four iterations
PC1 first principal component factor, *PC2* second principal component factor, *PC3* third principal component factor

different resources. PCA was performed based on the concentrations of all heavy metals and metalloids with varimax rotation (Table 7). The values of Kaiser-Meyer-Olkin and Bartlett were 0.761 (>0.6) and 148.226 ($d_f = 45, P = 0.000 < 0.001$), respectively, indicating that PCA can be applied in dimensionality decompositions. The PCA results revealed that the variability of heavy metals and metalloids can be expressed by three principal components that explained 87.309 % of the total variance (Table 7). The first principal component (PC1) accounting for 54.625 % of the total variance had strong positive loadings of all of the heavy metals and metalloids (>0.6), except Mn, which indicated that the PC1 should possibly be

anthropogenic activities, including industrial, agricultural, and urban (Han et al. 2014; Jiang et al. 2013; Liang et al. 2015; Mao et al. 2013; Zhu et al. 2013a). The second principal component (PC2) explained 21.006 % of the total variance and has negatively loaded Pb, Zn, Cu, and Cd. It was consistent with the results of I_{geo} , EF, mC_d , and RI that the four heavy metals severely contaminated the sampling sediments especially in Shuikoushan of Hengyang, Xiawan of Zhuzhou, and Yijiawan of Xiangtan and with that they are the main heavy metal pollutants of the current Zn–Pb mining and smelting technology in China (Qi et al. 2016). The third principal component (PC3) (11.678 % of total variance) only had a

Fig. 3. Dendrogram of hierarchical cluster analysis (HCA) to demonstrate the relationship between the ten heavy metals and metalloids in all sampling sediments of the Xiangjiang River, Hunan. Al was the reference element. Distance metrics were based on the Euclidean distance method and the Ward method



strong positive loading of Mn, implying that Mn originated from nature resource and/or Guangxi province (Liu et al. 2014). Hierarchical cluster analysis (HCA) generated similar results with PCC and PCA. As shown in Fig. 3, it was divided into two major clusters: (1) Pb, Cu, Zn, and Cd and (2) the rest of metals were further split into two subcluster: (i) Co, V, Ni, Cr, and Al and (ii) Mn and As, which indicated that the three groups of heavy metals and metalloids originated from different potential resources. The group (1) (Pb, Cu, Zn, and Cd) possibly originated from anthropogenic activities, especially from Pb–Zn mining and smelting industry. In the group (2), the subgroup (ii) (Mn and As) may be derived from Guangxi province (Liu et al. 2014) and the subgroup (i) (Co, V, Ni, Cr, and Al) possibly from nature resource because Al was the major natural element in the crust.

Conclusions

Heavy metal and metalloid pollutants in the Xiangjiang River have been a critical environmental concern in Hunan province in the last decades. To systematically and comprehensively investigate the contamination status and ecological risk of heavy metal and metalloid contamination in the river, the geoaccumulation index (I_{geo}), enrichment factor (EF), modified degree of contamination (mC_d), and potential ecological risk index (RI) were employed to assess the contamination status and potential ecological risk of heavy metals and metalloids in the surface sediments of the Xiangjiang River and the Pearson's correlation coefficient (PCC) analysis, principal component analysis (PCA) and hierarchical cluster analysis (HCA) were processed to identify the potential sources of the pollutants. The results showed that the mean concentrations of the ten heavy metals and metalloids in the sediment samples followed the order $Mn > Zn > Cr > V > Pb > Cu > As \approx Ni > Co > Cd$. I_{geo} , EF, mC_d , and RI revealed that Cd, followed by Pb, Zn, and Cu, caused severe contamination and posed very high potential ecological risk in the Xiangjiang River, especially in Shuikoushan of Hengyang, Xiawan of Zhuzhou, and Yijiawan of Xiangtan. PCC, PCA, and HCA indicated that Cd, Pb, Zn, and Cu possibly originated from Pb–Zn mining and smelting industry and clustered in the sampling sites Shuikoushan, Xiawan, and Yijiawan. Given that the contamination status and the potential ecological risk of Cd plus Pb, Zn, and Cu were severe in the Xiangjiang River, it is urgent to further research on their ecotoxicity to benthic organisms and efficient remediation to the contaminated sediments in the future.

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References

- Abraham GMS, Parker RJ (2008) Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environ Monit Assess* 136:227–238
- Acevedo-Figueroa D, Jiménez BD, Rodríguez-Sierra CJ (2006) Trace metals in sediments of two estuarine lagoons from Puerto Rico. *Environ Pollut* 141:336–342
- Akcay H, Oguz A, Karapire C (2003) Study of heavy metal pollution and speciation in Buyuk Menderes and Gediz river sediments. *Water Res* 37:813–822
- Audry S, Schäfer J, Blanc G, Jouanneau J-M (2004) Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). *Environ Pollut* 132:413–426
- Bednarova Z, Kuta J, Kohut L, Machat J, Klanova J, Holoubek I, Jarkovsky J, Dusek L, Hilscherova K (2013) Spatial patterns and temporal changes of heavy metal distributions in river sediments in a region with multiple pollution sources. *J Soils Sediments* 13:1257–1269
- Cao HC, Luan ZQ, Wang JD, Zhang XL (2009) Potential ecological risk of cadmium, lead and arsenic in agricultural black soil in Jilin Province, China. *Stoch Environ Res Risk Assess* 23:57–64
- Cheng QL, Wang RL, Huang WH, Wang WL, Li XD (2015) Assessment of heavy metal contamination in the sediments from the Yellow River Wetland National Nature Reserve (the Sanmenxia section), China. *Environ Sci Pollut Res* 22:8586–8593
- China National Environmental Monitoring Center (1990) The background concentrations of soil elements in China. China Environmental Science Press, Beijing
- Ciszewski D, Kubsik U, Aleksander-Kwaterczak U (2012) Long-term dispersal of heavy metals in a catchment affected by historic lead and zinc mining. *J Soils Sediments* 12:1445–1462
- Dung T, Cappuyns V, Swennen R, Phung N (2013) From geochemical background determination to pollution assessment of heavy metals in sediments and soils. *Rev Environ Sci Biotechnol* 12:335–353
- Feng H, Han XF, Zhang WG, Yu LZ (2004) A preliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization. *Mar Pollut Bull* 49:910–915
- Fu J, Zhao CP, Luo YP, Liu CS, Kyzas GZ, Luo Y, Zhao DY, An SQ, Zhu HL (2014) Heavy metals in surface sediments of the Jialu River, China: their relations to environmental factors. *J Hazard Mater* 270:102–109
- Ghrefat H, Abu-Rukah Y, Rosen M (2011) Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Kafra Dam, Jordan. *Environ Monit Assess* 178:95–109
- Hakanson L (1980) An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Res* 14:975–1001
- Han CN, Qin YW, Zheng BH, Ma YQ, Zhang L, Cao W (2014) Sediment quality assessment for heavy metal pollution in the Xiang-jiang River (China) with the equilibrium partitioning approach. *Environ Earth Sci* 72:5007–5018
- Heim S, Schwarzbauer J (2013) Pollution history revealed by sedimentary records: a review. *Environ Chem Lett* 11:255–270
- Hu BQ, Li J, Zhao JT, Yang J, Bai FL, Dou YG (2013) Heavy metal in surface sediments of the Liaodong Bay, Bohai Sea: distribution, contamination, and sources. *Environ Monit Assess* 185:5071–5083

- Jamshidi-Zanjani A, Saeedi M (2013) Metal pollution assessment and multivariate analysis in sediment of Anzali international wetland. *Environ Earth Sci* 70:1791–1808
- Jiang M, Zeng GM, Zhang C, Ma XY, Chen M, Zhang JC, Lu LH, Yu Q, Hu LP, Liu LF (2013) Assessment of heavy metal contamination in the surrounding soils and surface sediments in Xiawangang River, Qingshitang District. *PLoS One* 8:e71176
- Li F, Zeng XY, Wu CH, Duan ZP, Wen YM, Huang GR, Long XL, Li MJ, Li MJ, Xu JY (2013) Ecological risks assessment and pollution source identification of trace elements in contaminated sediments from the Pearl River Delta, China. *Biol Trace Elem Res* 155:301–313
- Liang J, Liu JY, Yuan XZ, Zeng GM, Lai X, Li XD, Wu HP, Yuan YJ, Li F (2015) Spatial and temporal variation of heavy metal risk and source in sediments of Dongting Lake wetland, mid-south China. *J Environ Sci Health Part A* 50:100–108
- Liao YP, Min XB, Yang ZH, Chai LY, Zhang SJ, Wang YY (2014) Physicochemical and biological quality of soil in hexavalent chromium-contaminated soils as affected by chemical and microbial remediation. *Environ Sci Pollut Res* 21:379–388
- Lin CY, He MC, Liu XT, Guo W, Liu SQ (2013) Contamination and ecological risk assessment of toxic trace elements in the Xi River, an urban river of Shenyang city, China. *Environ Monit Assess* 185:4321–4332
- Liu WX, Li XD, Shen ZG, Wang DC, Wai OWH, Li YS (2003) Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary. *Environ Pollut* 121:377–388
- Liu JL, Li YL, Zhang B, Cao JL, Cao ZG, Domagalski J (2009) Ecological risk of heavy metals in sediments of the Luan River source water. *Ecotoxicology* 18:748–758
- Liu J, Zhang XH, Li TY, Wu QX, Jin ZJ (2014) Soil characteristics and heavy metal accumulation by native plants in a Mn mining area of Guangxi, South China. *Environ Monit Assess* 186:2269–2279
- Mamat Z, Haximu S, Zhang ZY, Aji R (2016) An ecological risk assessment of heavy metal contamination in the surface sediments of Bosten Lake, northwest China. *Environ Sci Pollut Res* 23:7255–7265
- Mao LJ, Mo DW, Guo YY, Fu Q, Yang JH, Jia YF (2013) Multivariate analysis of heavy metals in surface sediments from lower reaches of the Xiangjiang River, southern China. *Environ Earth Sci* 69:765–771
- Müller G (1969) Index of geoaccumulation in sediments of the Rhine river. *J Geol* 2:108–118
- Nazeer S, Hashmi MZ, Malik RN (2014) Heavy metals distribution, risk assessment and water quality characterization by water quality index of the River Soan, Pakistan. *Ecol Indic* 43:262–270
- Pejman A, Nabi Bidhendi G, Ardestani M, Saeedi M, Baghvand A (2015) A new index for assessing heavy metals contamination in sediments: a case study. *Ecol Indic* 58:365–373
- Peluso L, Bulus Rossini G, Salibián A, Ronco A (2013) Physicochemical and ecotoxicological based assessment of bottom sediments from the Luján River basin, Buenos Aires, Argentina. *Environ Monit Assess* 185:5993–6002
- Qi J, Zhang H, Li X, Lu J, Zhang G (2016) Concentrations, spatial distribution, and risk assessment of soil heavy metals in a Zn-Pb mine district in southern China. *Environ Monit Assess* 188:1–11
- Shi XM, Wang JH (2013) Comparison of different methods for assessing heavy metal contamination in street dust of Xianyang City, NW China. *Environ Earth Sci* 68:2409–2415
- Tam NFY, Wong YS (2000) Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environ Pollut* 110:195–205
- Tang WZ, Shan BQ, Zhang H, Zhang WQ, Zhao Y, Ding YK, Rong N, Zhu XL (2014) Heavy metal contamination in the surface sediments of representative limnetic ecosystems in eastern China. *Sci Rep* 4:7152
- Varol M (2011) Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *J Hazard Mater* 195:355–364
- Wang F, Wang WX, Huang XP (2012) Spatial distribution of gut juice extractable Cu, Pb and Zn in sediments from the Pearl River Estuary, Southern China. *Mar Environ Res* 77:112–119
- Wang YY, Yang ZH, Peng B, Chai LY, Wu BL, Wu RP (2013) Biotreatment of chromite ore processing residue by *Pannonibacter phragmitetus* BB. *Environ Sci Pollut Res* 20:5593–5602
- Wang HT, Wang JW, Liu RM, Yu WW, Shen ZY (2015) Spatial variation, environmental risk and biological hazard assessment of heavy metals in surface sediments of the Yangtze River estuary. *Mar Pollut Bull* 93:250–258
- Yang Z, Wang Y, Shen Z, Niu J, Tang Z (2009a) Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. *J Hazard Mater* 166:1186–1194
- Yang ZF, Wang Y, Shen ZY, Niu JF, Tang ZW (2009b) Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. *J Hazard Mater* 166:1186–1194
- Yi YJ, Sun J, Tang CH, Zhang SH (2016) Ecological risk assessment of heavy metals in sediment in the upper reach of the Yangtze River. *Environ Sci Pollut Res* 23:11002–11013
- Zhang J, Liu CL (2002) Riverine composition and estuarine geochemistry of particulate metals in China—weathering features, anthropogenic impact and chemical fluxes. *Estuar Coast Shelf Sci* 54:1051–1070
- Zhang WG, Feng H, Chang JN, Qu JG, Xie HX, Yu LZ (2009) Heavy metal contamination in surface sediments of Yangtze River intertidal zone: an assessment from different indexes. *Environ Pollut* 157:1533–1543
- Zhao S, Feng CH, Wang DX, Tian CH, Shen ZY (2014) Relationship of metal enrichment with adverse biological effect in the Yangtze Estuary sediments: role of metal background values. *Environ Sci Pollut Res* 21:464–472
- Zhao DB, Wan SM, Yu ZJ, Huang J (2015a) Distribution, enrichment and sources of heavy metals in surface sediments of Hainan Island rivers, China. *Environ Earth Sci* 74:5097–5110
- Zhao Q, Zhou LM, Zheng XM, Wang YJ, Lu JM (2015b) Study on enzymatic activities and behaviors of heavy metal in sediment–plant at muddy tidal flat in Yangtze Estuary. *Environ Earth Sci* 73:3207–3216
- Zhu JY, Zhang JX, Li Q, Han T, Xie JP, Hu YH, Chai LY (2013a) Phylogenetic analysis of bacterial community composition in sediment contaminated with multiple heavy metals from the Xiangjiang River in China. *Mar Pollut Bull* 70:134–139
- Zhu XF, Ji HB, Chen Y, Qiao MM, Tang L (2013b) Assessment and sources of heavy metals in surface sediments of Miyun Reservoir, Beijing. *Environ Monit Assess* 185:6049–6062