

# Risk Assessment of Heavy Metal in the Surface Sediment at the Drinking Water Source of the Xiangjiang River in South China

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## Research

**Keywords:** Heavy metal, Risk assessment, Sediment, Distribution, The Xiangjiang River

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# 1 Risk Assessment of Heavy Metal in the Surface Sediment at the 2 Drinking Water Source of the Xiangjiang River in South China

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5

## 6 Abstract

7 **Background:** The Xiangjiang River is an important drinking water resource for the Hunan  
8 province of China. It is crucial to ascertain the pollution status, influencing factors, ecological  
9 risks, and possible sources of heavy metals in the sediments of the Xiangjiang River. Sediment is  
10 both a source and a sink of heavy metals in aquatic ecosystems. In this study, surface sediment  
11 was collected from the Zhuzhou Reach of the Xiangjiang River and eight heavy metals were  
12 investigated.

13 **Results:** In all sediment samples, all eight heavy metals were detected and their average  
14 concentration fell in the order of Zn > Pb > As > Cu > Cr > Ni > Cd > Co. Assessment shows  
15 extremely serious Cd pollution and a very high potential ecological risk from Cd. According to  
16 correlation analysis and principle component analysis (PCA), As, Cu, Ni, Pb, and Zn originate  
17 from industrial wastewater and mineral smelting activities, whereas Co, Cr, and Ni come from  
18 natural sources. Redundancy analysis (RDA) reveals that the organic matter content and the  
19 particle size of the sediment have a certain influence on the enrichment of heavy metals.

20 **Conclusion:** Among all eight examined heavy metals in the surveyed area, the content of Zn, Pb,  
21 and As is the highest, and that of Cd and Co is the lowest. Despite a low level of absolute content,  
22 the Cd in sediment already renders a high ecological risk and thus calls for urgent attention.  
23 Anthropogenic activities are the main source of heavy metals in the sediment. The distribution of  
24 heavy metals may also be influenced by sediment properties. The results provide guidance for  
25 controlling heavy metal pollution and protecting drinking water sources in the Xiangjiang River.

26 **Keywords:** Heavy metal, Risk assessment, Sediment, Distribution, The Xiangjiang River

## 27 **Background**

28 Heavy metals are a pressing concern in terms of their pollution in aquatic ecosystems because  
29 of their persistence, environmental toxicity, bioaccumulation, *etc.* [1-4]. Aquatic  
30 environments (e.g., lakes [5], rivers [6], reservoirs [7], and wetlands [8]) receive heavy metals  
31 in untreated or inadequately treated wastewater from domestic, industrial, and agricultural  
32 sources. Pollution from heavy metals is inflicting rivers worldwide [9, 10], especially in  
33 developing countries [11, 12].

34 As an important component in riverine ecosystems, sediment serves as both a sink and a  
35 source of heavy metals [13, 14]. Most heavy metals quickly deposit into the sediment after  
36 entering rivers, and are much more concentrated in the sediment than in the water body of  
37 riverine systems [15, 16]. Conversely, when the physicochemical or hydrological conditions  
38 change, heavy metals in the sediment may desorb or resuspend to cause secondary pollution  
39 in the water body [17, 18]. The accumulation of heavy metals in the sediment directly affects  
40 benthic organisms and also influences many other organisms through the food web [19, 20],  
41 and endangers the wellbeing of the aquatic ecosystem. Therefore, it is of great importance to  
42 assess and understand the distribution and accumulation of heavy metals in sediment.

43 The Xiangjiang River is a major tributary of the Yangtze River and a key river in South China.  
44 It flows through the Hunan province and supports many densely populated cities, providing  
45 services to both industry and agriculture [21, 22]. Unfortunately, the Xiangjiang River has  
46 become one of the most seriously polluted rivers **by heavy metals** in China over the past few  
47 decades because of the wastewater discharge from mining and metallurgical industries  
48 carrying heavy metals [23]. Although many researchers have studied heavy metal pollution in  
49 the Xiangjiang River [24-26], a systematic study is still lacking to associate the sediment with  
50 the distribution, characteristics, risk assessment, possible sources, and impact of heavy  
51 metals.

52 The Zhuzhou Reach of the Xiangjiang River is a typical area polluted by heavy metals [27].

53 In this work, we collected 30 surface sediment samples from the Zhuzhou Reach of the  
54 Xiangjiang River in order to (1) characterize the occurrence and distribution of eight heavy  
55 metals (Cd, As, Pb, Zn, Cu, Ni, Cr, and Co) in the sediment, (2) assess the pollution status  
56 and the ecological risk of the heavy metals, (3) identify possible sources of heavy metal  
57 pollution from principle component analysis (PCA) and Pearson's correlation analysis, and (4)  
58 use redundancy analysis (RDA) to analyze the sediment characteristics that influence heavy  
59 metal distribution. The results illuminate on the environmental behavior of heavy metals and  
60 provide a reference for controlling pollution and ecological remediation in nearby areas and  
61 similar riverine systems.

## 62 **Materials and methods**

### 63 *Study area and sample collection*

64 The Xiangjiang River is the second largest tributary of the Yangtze River and an important  
65 drinking water source in South China. The main channel of the river is 856 km long, and its  
66 basin covers 94721 km<sup>2</sup> and supports >30 million residents of the Hunan Province [28]. It  
67 flows from south to north en route 6 major cities in Hunan, *i.e.*, Yongzhou, Hengyang,  
68 Zhuzhou, Xiangtan, Changsha, and Yueyang, and finally joins the Yangtze River via the  
69 Dongting Lake. The Hunan Province is known as the “Nonferrous Metal Village” because of  
70 its abundant mineral resources (e.g., Cd, Zn, Pb, Cu, *etc.* [29]). However, the mining and  
71 smelting of nonferrous metals over the past years caused severe heavy metal pollution to the  
72 Xiangjiang River. The city of Zhuzhou at the east of the Hunan Province is at the lower  
73 reaches of the Xiangjiang River. The area is rich in mineral resources and active in mining,  
74 ore smelting, and other major industrial practices. Therefore, we chose the Zhuzhou Reach of  
75 the Xiangjiang River for pollution evaluation and risk assessment. At the upstream of the  
76 surveyed area, there are many companies producing Zn, Pb, As, and alloys as well as other  
77 companies that carry out comprehensive recovery of Cu, Au, Ag, Bi, Te, Cd, In, and other  
78 rare metals. In this work, eight target heavy metals (Cd, As, Pb, Zn, Cu, Ni, Cr, and Co) were

79 chosen for evaluation after examining the actual situation of the study area and consulting  
80 literatures on heavy metals in the Xiangjiang River [21, 25, 28].

81 Ten sampling transects (S1–S10) were selected from upstream to downstream in the  
82 investigated area (Fig. 1). Surface sediment samples (1 kg) were collected in August, 2011  
83 with a core sampler at the north side, in the middle, and at the south side of the river from the  
84 top 5 cm layer of the riverbed. Each sample consists of a mixture of three samples from one  
85 sampling site. The collections from each transect were stored in acid-rinsed polyethylene  
86 plastic bags and transported immediately to the laboratory for storage at  $-20\text{ }^{\circ}\text{C}$  until further  
87 analysis, all sediment samples were analyzed within a week.

88

89 **Fig. 1** Map of the Xiangjiang River Basin and the sampling sites.

90

### 91 *Sample treatment and analysis*

92 Heavy metals in the sediment samples were determined at the Chinese Academy of  
93 Environmental Sciences according to published protocols [30, 31]. Briefly, crude sediment  
94 samples were freeze-dried, finely ground, homogenized, and sieved (100 mesh,  $150\text{ }\mu\text{m}$ ). The  
95 prepared sample (0.05 g) was digested with mixed acid (5 mL HCl, 3 mL HNO<sub>3</sub>, 7 mL HF,  
96 0.25 mL HClO<sub>4</sub>) in a Teflon beaker. After the digestion, the dissolved sample was diluted  
97 with 2% HNO<sub>3</sub>, and the concentrations of heavy metals were analyzed using inductively  
98 coupled plasma mass spectrometry (ICP-MS, Agilent 7500 series, USA). The recoveries of  
99 standard reference metals were 90%–110%. For more details, refer to Lin et al. [32]. The  
100 content of organic matters (OM) in the sediment was determined according to the standard  
101 methods for soil analysis [33]. Grain size was measured by a laser scattering particle size  
102 distribution analyzer (LA-300, Horiba, Kyoto, Japan) to determine the median sediment size  
103 ( $D_{50}$ ) and the fine particle ( $<63\text{ }\mu\text{m}$ ) content.

104 All reagents and solvents used in the sediment analysis were of analytical grade. The  
105 analytical procedure conformed to the certified standards of GBW07309 (China Stream  
106 Sediment Reference Materials). The results were within the acceptable level of uncertainty  
107 given by certified values.

## 108 *Pollution assessment of heavy metals*

### 109 *Geoaccumulation*

110 The geoaccumulation index ( $I_{geo}$ ) formulated in 1969 is now one of the most widely used  
111 measures to evaluate heavy metal pollution in sediment because it can directly reflect the  
112 enrichment of exogenous heavy metals and provides consistent and comparable data [34, 35].

113 It is calculated as follows:

$$114 \quad I_{geo} = \text{Log}_2 \left( \frac{C_{\text{sample}}}{1.5 C_{\text{background}}} \right) \quad (1)$$

115 where  $C_{\text{sample}}$  is the concentration of the heavy metal in the sediment sample and  $C_{\text{background}}$  is  
116 the geochemical background concentration ( $\text{mg kg}^{-1}$ ) of the heavy metal. A background  
117 matrix correction factor of 1.5 is adopted as a coefficient to compensate for weathering and  
118 lithogenic effects. Table 2 lists the background concentration of the investigated heavy metals  
119 in the Dongting Lake **sediments** [36]. Pollution can be classified into seven classes based on  
120 the  $I_{geo}$  value: Class 0 ( $I_{geo} \leq 0$ ), practically unpolluted; Class 1 ( $0 < I_{geo} \leq 1$ ), unpolluted to  
121 moderately polluted; Class 2 ( $1 < I_{geo} \leq 2$ ), moderately polluted; Class 3 ( $2 < I_{geo} \leq 3$ ),  
122 moderately to heavily polluted; Class 4 ( $3 < I_{geo} \leq 4$ ), heavily polluted; Class 5 ( $4 < I_{geo} \leq 5$ ),  
123 heavily to extremely polluted; Class 6 ( $I_{geo} > 5$ ), extremely polluted [37].

### 124 *Assessment of potential ecological risk*

125 The potential ecological risk index (RI) formulated by Hakanson in 1980 was used here to  
126 quantify the level of ecological risk of heavy metals in sediment [38]. The RI assesses the  
127 combined ecological and environmental toxicity to provide an overall evaluation of the  
128 potential risks of heavy metal pollution, and is calculated as follows:

129 
$$E_r^i = T_r^i \frac{C_{\text{sample}}}{C_{\text{background}}} \quad (2)$$

130 
$$RI = \sum E_r^i \quad (3)$$

131 where  $E_r^i$  and  $T_r^i$  are the potential ecological risk factor and the toxic response factor of the  
 132 heavy metal, respectively, and  $C_{\text{sample}}$  and  $C_{\text{background}}$  are the measured and background  
 133 concentration. The  $T_r^i$  values for Co, Cd, Ni, Cr, Cu, As, Pb, and Zn, all taken from literature,  
 134 are 5, 30, 5, 2, 5, 10, 5, and 1, respectively [39]. Table 1 lists the criteria for  $E_r^i$  and RI.

135 **Table 1.** Levels of potential ecological risk for heavy metal in sediments.

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

136

137 **Statistical analysis**

138 PCA and RDA were performed using Canoco 5.0 (Biometris, Netherlands). Pearson's  
 139 correlation analysis was conducted using SPSS 20.0 (SPSS Inc., Chicago, IL, USA). Data  
 140 analyses and statistical tests were performed using Microsoft Excel 2010.

141 **Results and discussion**

142 ***Occurrence and abundance of heavy metals in surface sediment***

143 Table 2 summarizes the minimum, maximum, and average concentrations (represented by dry  
 144 weight) of the eight heavy metals in the surface sediment samples from the Zhuzhou Reach of  
 145 the Xiangjiang River. All eight heavy metals were detected in all sediment samples. The  
 146 concentration of Cr, Co, Ni, Cu, Zn, As, Cd, and Pb ranged in 23.11–94.84, 5.26–25.24,  
 147 16.58–53.58, 20.54–159.3, 58.24–629.60, 34.74–186.80, 2.10–62.59, and 38.19–246.20 mg

148  $\text{kg}^{-1}$ , respectively. The average concentration ranked in the order of Zn ( $257.17 \text{ mg kg}^{-1}$ ) >  
 149 Pb ( $102.52 \text{ mg kg}^{-1}$ ) > As ( $98.38 \text{ mg kg}^{-1}$ ) > Cu ( $71.29 \text{ mg kg}^{-1}$ ) > Cr ( $59.71 \text{ mg kg}^{-1}$ ) > Ni  
 150 ( $36.29 \text{ mg kg}^{-1}$ ) > Cd ( $23.31 \text{ mg kg}^{-1}$ ) > Co ( $16.97 \text{ mg kg}^{-1}$ ). With the sediment of the  
 151 Dongting Lake taken as the background and a reference point, the concentration of the heavy  
 152 metals is 1.65–70.64 times higher in the sediment of the Zhuzhou Reach, thus indicating  
 153 remarkable pollution. In particular, Zn and Pb have higher concentration than other heavy  
 154 metals, which is consistent with the Pb–Zn smelting activities around the Zhuzhou city. The  
 155 lower concentration of other heavy metals is probably related to a less amount of discharge.

156 Table 2 also summarizes the concentration of the examined heavy metals in other reaches of  
 157 the Xiangjiang River and in other rivers in South China [28, 36, 40-42]. The distribution of  
 158 heavy metals is clearly different among different reaches of the Xiangjiang River (including  
 159 Yongzhou, Hengyang, Zhuzhou, and Changsha). The Yongzhou Reach is the upstream and  
 160 has the lowest concentration of heavy metals (except for Cr) in sediment [28]. The Hengyang  
 161 Reach is located between Yongzhou and Zhuzhou and has the highest concentration of Cu, Zn,  
 162 As, and Pb in sediment [40]. For the Zhuzhou Reach, the concentration of Co, Ni in the  
 163 sediment is generally lower, but the concentration of Cd is the highest. The Changsha Reach  
 164 is the downstream and does not have a heavy metal with particularly high or low  
 165 concentration [28]. The distinct distribution of different heavy metals may be associated with  
 166 specific local mining activities. However, the sediment of the Xiangjiang River is clearly  
 167 more polluted by heavy metals than the sediment of other rivers in South China, including the  
 168 Jinjiang River, Hanjiang River, and Yangtze River [41, 42]. The concentration of Zn seems to  
 169 be the highest among the examined heavy metals for all rivers, possibly due to regional Zn  
 170 production. This high level of Zn is not specific to Hunan. In fact, for the past 20 years in  
 171 China, Zn has an annual production higher than all seven other heavy metals except Cu [43].

172 **Table 2.** Concentration of heavy metals ( $\text{mg kg}^{-1}$ ) in the sediment of the Xiangjiang River  
 173 and of other rivers in South China.

Cr	Co	Ni	Cu	Zn	As	Cd	Pb	Ref.
----	----	----	----	----	----	----	----	------

	Zhuzhou Reach (n=30)	23.11	5.26	16.58	20.54	58.24	34.74	2.1	38.19	
	Minimum									
	Zhuzhou Reach Maximum	94.84	25.24	53.58	159.3	629.60	186.80	62.59	246.20	This study
Xiangjiang River	Zhuzhou Reach Average	59.71	16.97	36.29	71.29	257.17	98.38	23.31	102.52	
	Yongzhou Reach (n=8)	129.25	30.88	107.38	51.58	71.85	51.90	6.825	93.80	[28]
	Hengyang Reach (n=8)	54.59	/	/	112.1	659.7	135.2	21.66	359.4	[40]
	Changsha Reach (n=12)	95.10	19.45	48.70	73.13	465.7	/	13.63	140.10	[28]
	Jinjiang River (n=8)	7.63	1.88	2.80	7.24	48.09	40.96	0.07	32.79	[41]
	Hanjiang River (n=6)	16.24	3.39	12.94	9.28	62.47	59.48	0.10	26.97	[41]
	Yangtze River (n=34)	82.87	/	32.85	25.14	82.92	9.31	0.17	25.13	[42]
Dongting Lake (Background)	44	10.3	21.2	20	83.3	15	0.33	23.3	[36]	

174

175 *Spatial distribution of heavy metals*

176 Fig. 2 illustrates the concentration of the heavy metals at S1–S10. The total concentration of  
 177 heavy metals gradually increases as the water flows through the Zhuzhou Reach and peaks at  
 178 S6 (1042.00 mg kg<sup>-1</sup>), then suddenly decreases sharply at S7 to only 280.33 mg kg<sup>-1</sup>, but rises  
 179 again to about 650 mg kg<sup>-1</sup> at the downstream sites S8–S10. Zn has the highest concentration  
 180 at S6 (435.84 mg kg<sup>-1</sup>) and then the next highest at S5 (127.04 mg kg<sup>-1</sup>). There is no  
 181 significant difference in the concentrations of heavy metals within the upstream (S1–S4) and  
 182 within the downstream (S8–S10), but there is a significant difference within the midstream  
 183 (S5–S7).

184

185 **Fig. 2** Spatial distribution of heavy metals in the sediment of the Zhuzhou Reach.

186

187 The concentration of heavy metals is the highest at S6, possibly due to the discharge of local  
188 pollution sources. Other factors such as the grain size and the OM content of sediment can  
189 also affect the concentration of heavy metals. For instance, sediment with a higher content of  
190 OM adsorbs more heavy metals [44]. Indeed, Table S1 shows that the OM content of S6 is the  
191 highest among all sites. In fact, S6 is located in the middle of the surveyed area and there is a  
192 sandbar between S6 and S7. This geographic feature may increase the deposition of particles  
193 carrying heavy metals into the sediment of S6.

194

195 **Fig. 3** Heavy metal concentration in the sediment collected at the south side, the north side,  
196 and in the middle of the river.

197

198 Most heavy metals have slightly higher concentration in the middle of the river than on the  
199 south side, and all heavy metals have significantly higher concentrations on the north side  
200 (Fig. 3). In particular, the concentration of Zn and Pb in the north is nearly twice as much as  
201 in the middle and the south. The asymmetrical concentration can be associated with the  
202 nonferrous metal mining and smelting plants in the north that produce Zn, Pb, and alloys and  
203 discharge substantial amount of wastewater.

#### 204 *Assessment of heavy metal pollution*

205 Many measures have been used in literature to assess heavy metal pollution in sediment, e.g.,  
206 the geoaccumulation index, the potential ecological risk index, the enrichment factor, *etc.*  
207 [45-47]. In this study, we used  $I_{geo}$  and RI to assess heavy metal pollution in the sediment of  
208 the Zhuzhou Reach with reference to the concentration of Dongting Lake sediments as the  
209 background.

210 *Assessment of I<sub>geo</sub>*

211 Fig. 4a shows a boxplot of the average  $I_{geo}$  values for the eighty heavy metals, which can be  
212 ranked in descending order as follows: Cd (5.01) > As (1.94) > Pb (1.40) > Zn (0.74) > Ni  
213 (0.11) > Co (0.04) > Cu (0.43) > Cr (-0.26). The pollution levels of the metals are thus  
214 segmented into 4 classes according to the  $I_{geo}$  values. That is, the Zhuzhou Reach is extremely  
215 polluted by Cd (class 6), moderately to heavily polluted by As and Pb (class 2), unpolluted to  
216 moderately polluted by Zn, Ni, Co, and Cu (class 1), and practically unpolluted by Cr (class  
217 0).

218 The different colors in Fig. 4b denote the class of  $I_{geo}$  for each heavy metal at S1–S10. The  
219 pollution of Cd is highly variable geographically, from Class 3 (S7) up to Class 6 (S3–S6, S8,  
220 S10). The pollution of As and Pb varies from Class 1 to Class 3, and the pollution of all other  
221 metals stay within two neighboring classes. The pollution of Cr, Co, and Ni appears to be  
222 mild (Class 0 Cr for 60%, Class 1 Co for 70%, Class 1 Ni for 80% of the 10 sites). Pollution  
223 is more severe midstream (S5–S7) and downstream (S8–S10) than upstream (S1–S4).

224

225 **Fig. 4** Box diagram of  $I_{geo}$  values of heavy metals (a), and pollution classies in different sites  
226 (b) in the sediment of the Zhuzhou Reach.

227

228 *Assessment of potential ecological risk*

229 Table S2 lists the calculated  $E_r^i$  values of the heavy metals, from which the RI values were  
230 derived (Fig. 5). The RI value of the whole surveyed area ranged from 422.31 to 4854.41,  
231 with an average of 2246.64, thus indicating high ecological risk (Table 1) from heavy metal  
232 pollution. The sediment of S7 has  $RI > 300$ , and all others even have  $RI > 600$  (Fig. 5).

233 Among the tested metals, Cd creates very high ecological risk to the sediment at all sites ( $E_r^i >$   
234 320). The level of single metal ecological risk of As is the lowest at S7 ( $E_r^i = 28.84$ ),

235 considerable at S5, S6, and S10, and moderate at all other sites. Other heavy metals (Pb, Cu,  
236 Ni, Co, Zn, and Cr) have low ecological risk in all sediments ( $E_r^i < 40$ ).

237

238 **Fig. 5** RI values of heavy metals in the sediment (derived from the  $E_r^i$  values).

239

#### 240 *Identification of the sources of heavy metals*

241 Analyzing the sources of heavy metals can help understand their distribution. Principal  
242 components analysis (PCA) and Pearson's correlation analysis were used to analyze the  
243 relationship and source of the heavy metals [28, 48].

244 In this study, PCA was performed based on the determined concentrations of heavy metals  
245 with varimax rotation. The Kaiser–Meyer–Olkin (KMO) test gives 0.76 ( $> 0.7$ ) and Bartlett  
246 test gives 397.58 (df = 28,  $p < 0.001$ ), both indicating strong correlation among variables and  
247 confirming that PCA can be used to reduce the dimensionality of variables. In the PCA results  
248 (Fig. 6 and S1), PC1 accounts for 51.30% of the variation, and its representative congeners  
249 include Cd, Zn, As, Cu, and Pb, implying a common source that is possibly exogenous  
250 discharge [24, 49]. This speculation is further supported by the Pearson's correlation analysis  
251 (Fig. 7), in which all heavy metals are significantly positively correlated with each other ( $r >$   
252  $0.60$ ,  $p < 0.01$ ). Note that Pb and Zn, the main pollutants of the current Pb–Zn mining and  
253 smelting industry in China [50, 51], have a particularly high correlation ( $r = 0.95$ ,  $p < 0.01$ ).  
254 The PC2 accounts for 39.85% of the variation, and its representative congeners include Co,  
255 Ni, and Cr. The PCA results also indicate that at sites5, the sediment at north side is affected  
256 by Cd, Zn, As, Cu, Pb (Fig. S1), while the sediment the middle of river is mainly affected by  
257 Co, Ni, and Cr. It may be due to the effects of hydrodynamics or other sources, in the  
258 pollution assessment, Cr, Ni, and Co all have lower  $I_{geo}$  and lower  $E_r^i$ . Therefore, they may  
259 have been derived from natural processes such as soil erosion and rock weathering. This  
260 hypothesis is also supported by previous study [28, 46].

261

262 **Fig. 6.** PCA diagram of tested heavy metals in the sediment of different sampling sites.

263

264

265 **Fig. 7** Pearson's correlation coefficients ( $r$ ) of heavy metals and environmental factors in the  
266 sediment of the Zhuzhou Reach.

267

### 268 *Effects of environmental variables on the heavy metals*

269 Many environmental factors affect the distribution of heavy metals in sediment. The  
270 redundancy analysis (RDA) was used here to further investigate the environmental variables  
271 that affect the distribution of heavy metal. The considered environmental variables include the  
272 organic matter content (OM), median size ( $D_{50}$ ), and fine particle content (grain size < 63  $\mu\text{m}$ )  
273 of the sediment samples (Table S1). In the RDA result (Fig. 8), the angle between the  
274 environmental variable and the heavy metal reflects their relevance. The concentrations of  
275 heavy metal are positively correlated to OM, *i.e.*, sediment with relatively high OM tends to  
276 be more polluted by heavy metals. It was previously suggested that OM in sediment can  
277 adsorb heavy metals from the environment [52]. The grain size distribution of sediment is  
278 also an important factor that affects the enrichment of heavy metals [53]. Sediment particles  
279 can adsorb heavy metals by both physical and chemical processes. Physical adsorption is  
280 mainly related to the specific surface area of the sediment, and a smaller particle size of the  
281 sediment gives larger surface area and thus stronger adsorption capacity. Chemical adsorption  
282 is related to the active components contained in sediment particles, and the sediment tends to  
283 adsorb a greater amount of active components when it has smaller particle size [44, 54, 55].  
284 Therefore, heavy metals are generally negatively correlated with  $D_{50}$ . The fine particle content  
285 (grain size < 63  $\mu\text{m}$ ) has influences on the heavy metal concentration. Fig. 7 also shows the  
286 correlation between the environmental variables and the heavy metals.

287

288 **Fig. 8** Redundancy analysis diagram between heavy metals and sediment variables.

289

## 290 **Conclusions**

291 Heavy metal pollutants in river sediment have been a serious environmental concern in  
292 aquatic ecosystems. This study examines eight heavy metals in the surface sediment of the  
293 Zhuzhou Reach of the Xiangjiang River. All eight heavy metals were detected at all sampling  
294 sites, with a concentration higher than the background value. Their average concentration fell  
295 in the order of Zn > Pb > As > Cu > Cr > Ni > Cd > Co. Pollution appeared more serious in  
296 the midstream and on the northern side of the Xiangjiang River, possibly due to point source  
297 pollution nearby. Among the selected heavy metals, Cd presents very high ecological risk and  
298 should be carefully monitored and remediated. Most other heavy metals incur limited, if any,  
299 pollution according to the risk assessment. It was found from PCA and correlation analysis  
300 that Pb, Zn, As, Cu, and Cd are mainly originated from anthropogenic activities (industrial  
301 wastewater and mineral exploitation) whereas Cr, Co, and Ni can be attributed to the release  
302 from natural sources. Organic matter and grain size are the main factors affecting the  
303 distribution of heavy metals in the sediment, and heavy metals become enriched in the  
304 sediment when its organic matter is higher and particle size is smaller.

## 305 **Abbreviations**

306 PCA principle component analysis

307 RDA redundancy analysis

308  $I_{geo}$  geoaccumulation index

309 RI potential ecological risk index

310 OM organic matters

311  $D_{50}$  median size

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313 None applicable.

314 **Authors' contributions**

315 ZH and XZ were involved in the experiments and manuscript writing. ZH were responsible  
316 for the data analysis. CL and JD collected samples. ZH and BZ designed the study. XZ and  
317 BZ contributed to correction of the manuscript. All authors read and approved the final  
318 manuscript.

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322 **Availability of data and materials**

323 The datasets obtained and analyzed in the current study are available from the  
324 corresponding author on reasonable request.

325 **Ethics approval and consent to participate**

326 Not applicable.

327 **Consent for publication**

328 Not applicable.

329 **Competing interests**

330 The authors declare that they have no competing interests.

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# Figures

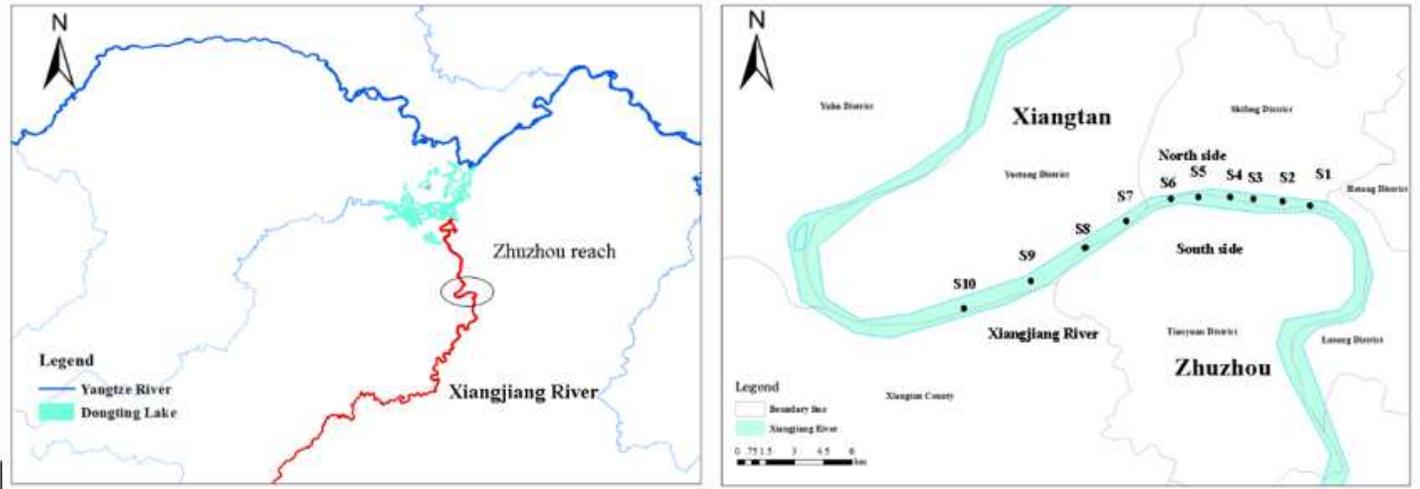
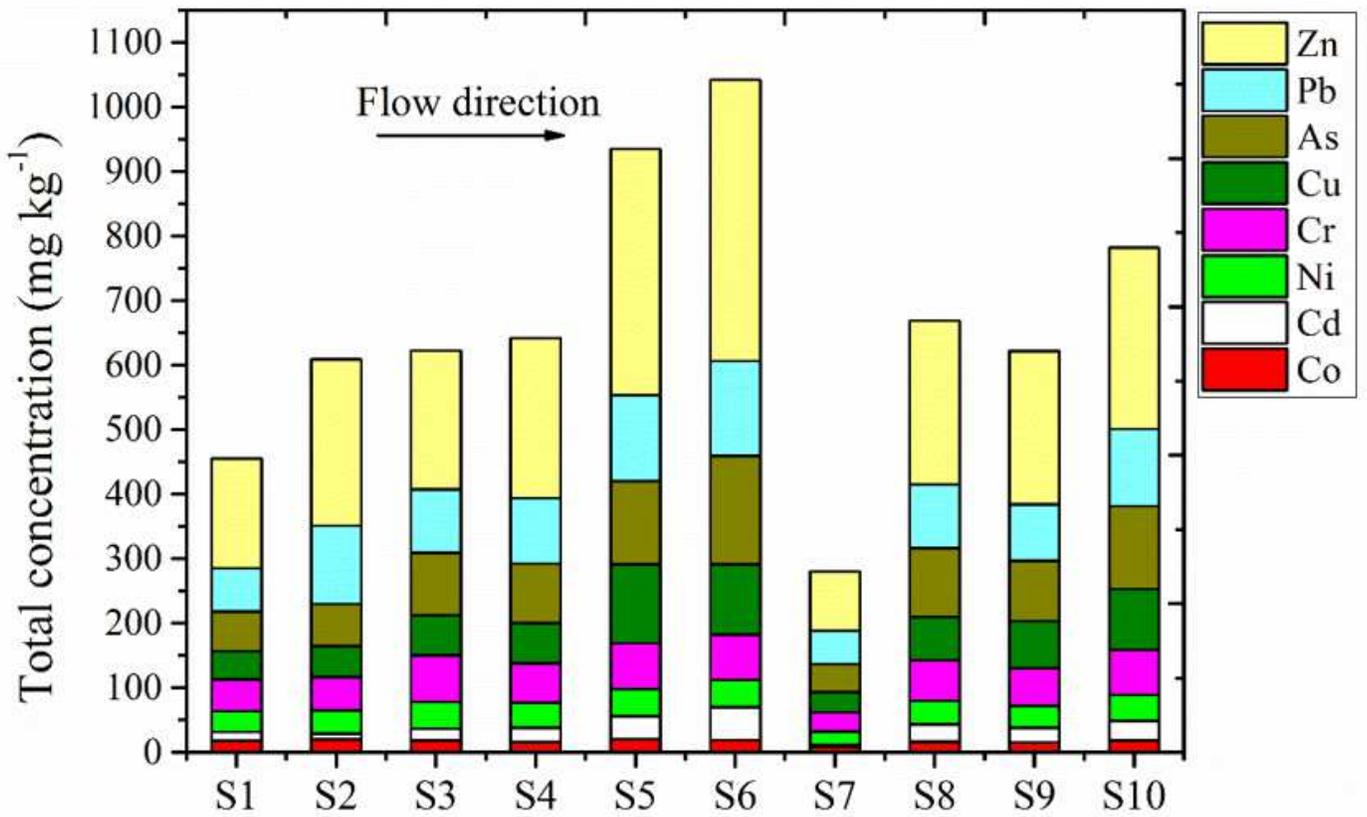


Figure 1

Map of the Xiangjiang River Basin and the sampling sites. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.



**Figure 2**

Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

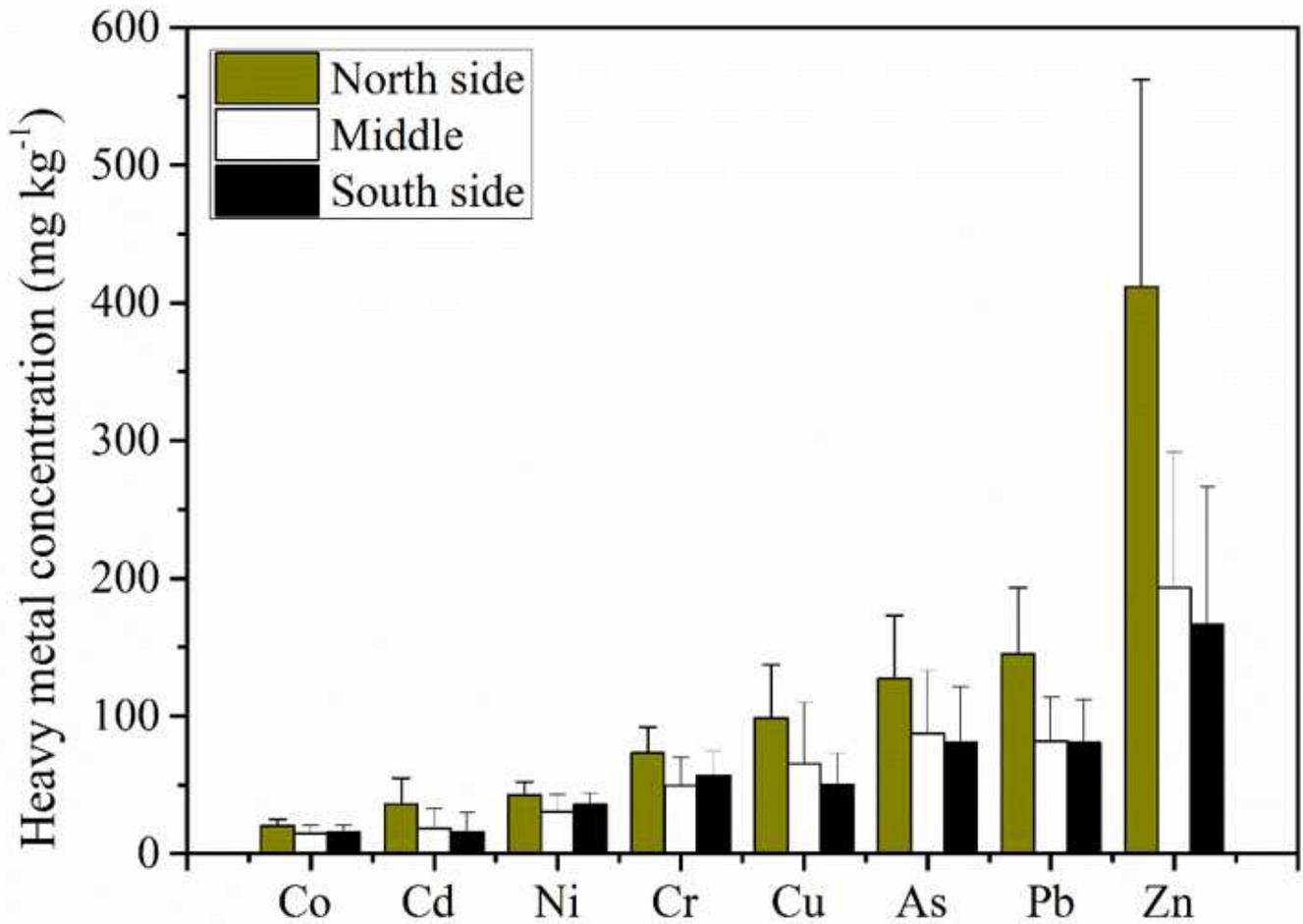
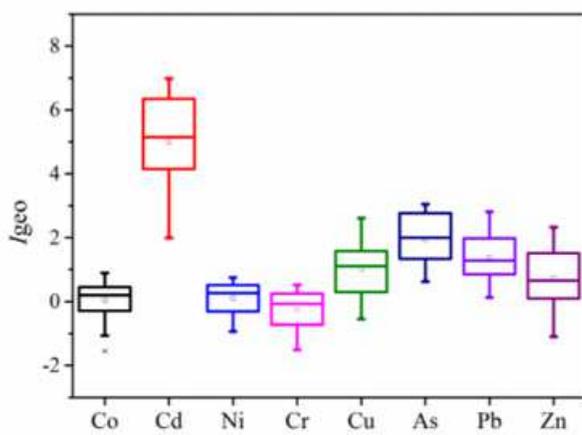


Figure 3

Heavy metal concentration in the sediment collected at the south side, the north side, and in the middle of the river.



a

$I_{geo}$	Co	Cd	Ni	Cr	Cu	As	Pb	Zn	Class
S1	0.19	4.64	-0.07	-0.50	0.42	1.37	0.82	0.23	0
S2	0.27	3.82	0.09	-0.47	0.42	1.46	1.44	0.54	1
S3	0.26	5.10	0.36	0.12	1.02	2.09	1.44	0.69	2
S4	-0.02	5.47	0.21	-0.16	1.05	2.03	1.52	0.97	3
S5	0.29	5.66	0.32	0.02	1.56	2.29	1.82	1.30	4
S6	0.28	6.67	0.39	0.04	1.79	2.89	2.06	1.75	5
S7	-0.99	2.81	-0.69	-1.18	0.05	0.92	0.54	-0.55	6
S8	0.05	5.20	0.16	-0.15	0.96	2.11	1.40	0.73	
S9	-0.16	4.94	0.02	-0.28	1.23	1.81	1.19	0.70	
S10	0.21	5.76	0.30	0.04	1.61	2.43	1.72	1.06	

b

Figure 4

Box diagram of Igeo values of heavy metals (a), and pollution classes in different sites (b) in the sediment of the Zhuzhou Reach.

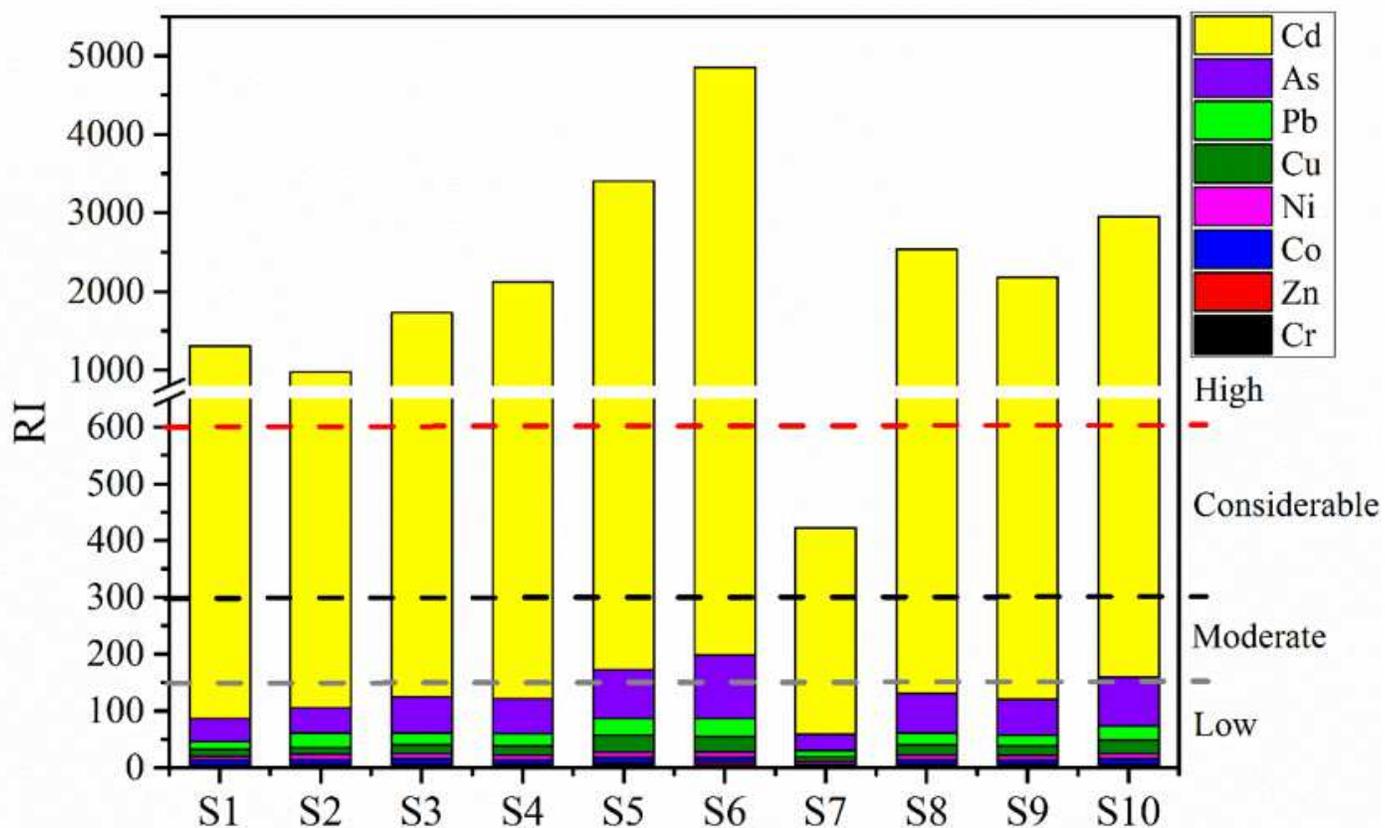
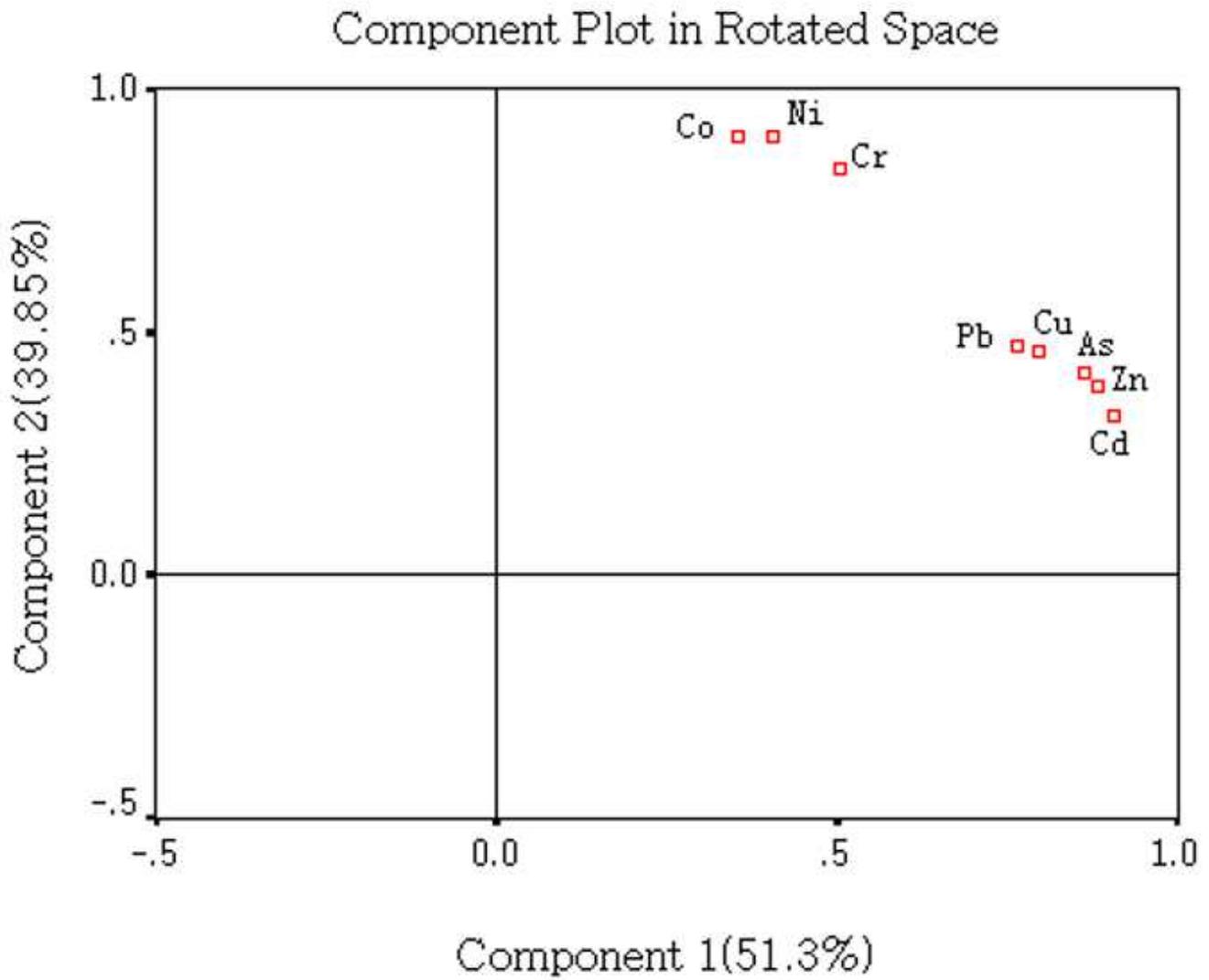


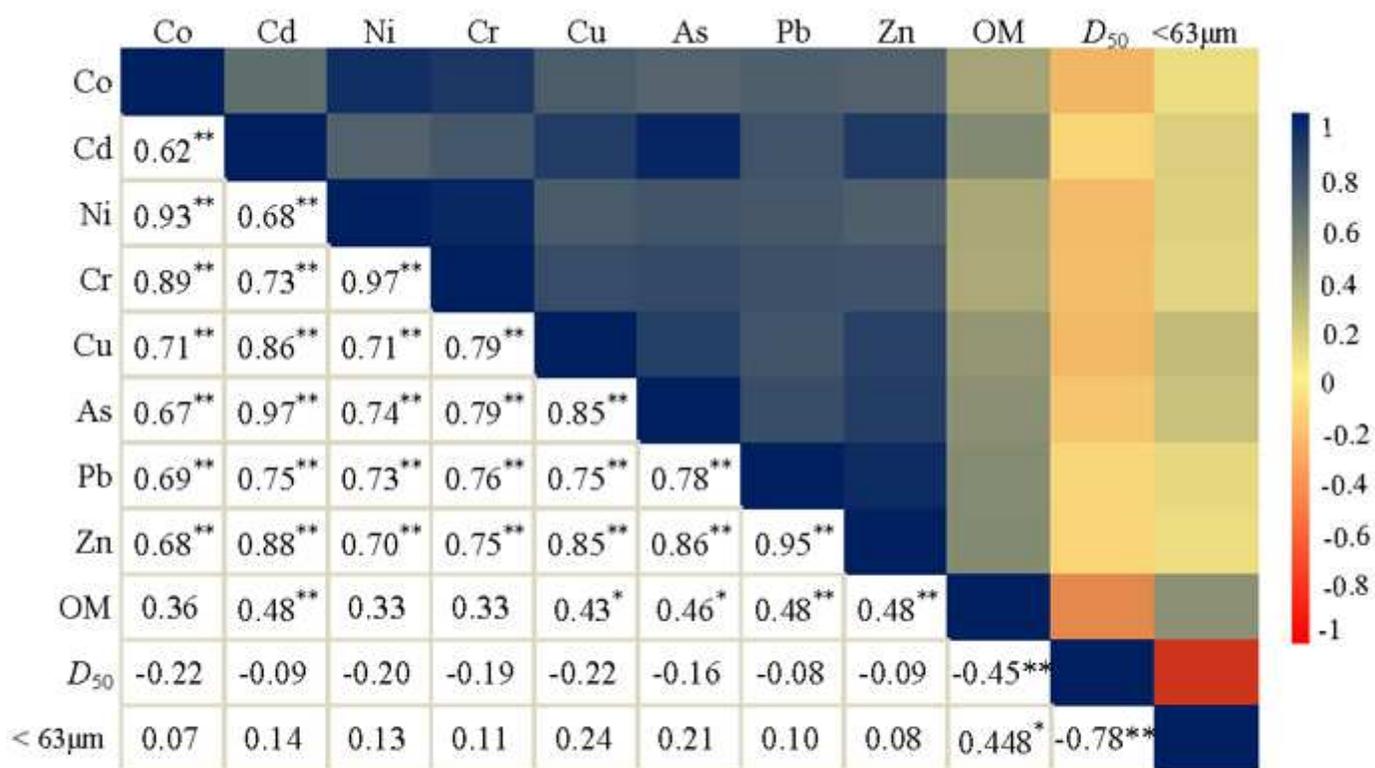
Figure 5

RI values of heavy metals in the sediment (derived from the values)



**Figure 6**

Principal component profile of heavy metals in the sediment of different sampling sites..



\* Correlation is significant at the 0.05 level (two-tailed),  
 \*\* Correlation is significant at the 0.01 level (two-tailed).

**Figure 7**

Pearson's correlation coefficients (r) of heavy metals and environmental factors in the sediment of the Zhuzhou Reach.

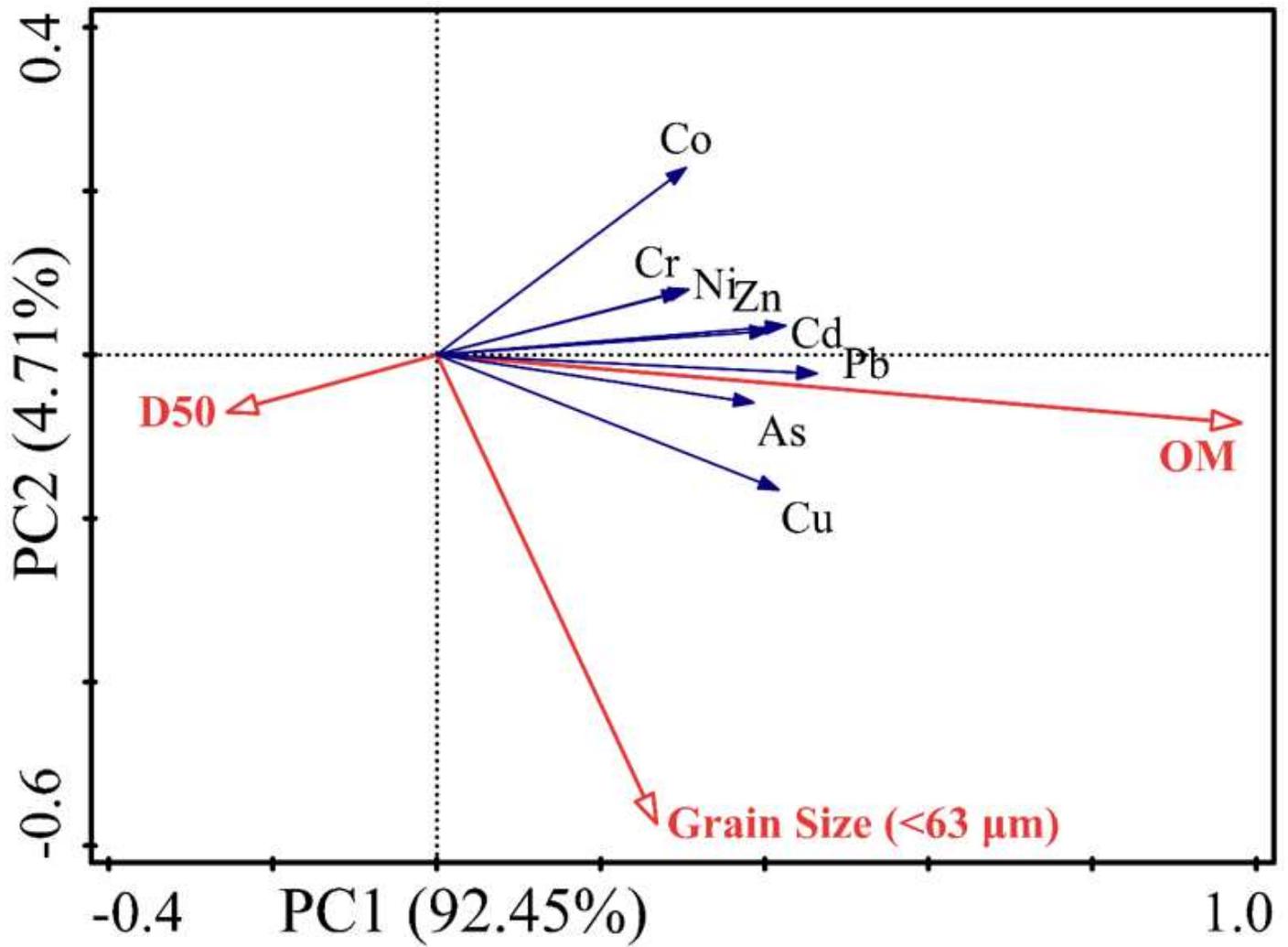


Figure 8

Redundancy analysis diagram between heavy metals and sediment variables.

## Supplementary Files

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