

Assessment of heavy metal pollution in sediments from Xiangjiang River (China) using sequential extraction and lead isotope analysis

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Abstract: The heavy metal (such as Cr, Ni, Cu, Cd, Pb, and Zn) concentration, speciation, and pollution source in 43 sediment samples from the Xiangjiang River were investigated using sequential extraction combined with Pb isotope analysis. Cu, Cd, Pb, and Zn concentrations are higher than their background values, while Cr and Ni concentrations are close to those. Sequential extraction demonstrates that heavy metals have different fractions, showing different bioavailabilities. The $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio increases with decreasing bioavailability in the order of exchangeable<carbonate≈Fe-Mn oxides≈organic<residual ($p<0.05$). Wastewater, dust, and slag from mining and smelting areas, and the residual Pb are assumed to be the primary anthropogenic and natural sources of Pb, respectively. The percentages of anthropogenic Pb in the exchangeable, carbonate, Fe-Mn oxides, and organic fractions are (91.5±16.7)%, (61.1±13.9)%, (57.4±11.1)%, and (55.5±11.2)%, respectively, suggesting a significant input of anthropogenic Pb in these four fractions.

Key words: sediment; heavy metals; sequential extraction; lead isotope

1 Introduction

Heavy metal pollution is one of the greatest threats to environmental quality and human health because of the toxicity, persistence, non-degradability, and the bioaccumulation of heavy metals in the environment [1–3]. It is well recognized that heavy metals from industrial, urban, and agricultural sources that are introduced into rivers will be ultimately combined with sediments and become immobilized [1–2, 4]. However, when the environmental conditions change, heavy metals in sediments can be released into the water, thus causing potential ecological risks to the aquatic system [5–8]. Consequently, sediments are the main repositories of heavy metals and act as both carriers and potential pollution sources [6, 9–10]. For example, ZOOMIS et al [10] investigated the change in heavy metal mobility in sediments stored at different conditions (anoxic or oxic) and found that oxic conditions caused considerable amounts of heavy metals to be immobilized and, therefore, bioavailable.

Given the complexity of heavy metals in sediments, total metal concentration alone is not sufficient to evaluate the environmental influence of polluted

sediments. Heavy metals in sediments are retained by various mechanisms (ion exchange, adsorption, and precipitation or co-precipitation) and thus exist in different fractions [11]. Many sequential extraction schemes using different chemical reagents and experimental conditions have been developed for determining the speciation of heavy metals [12–14]. Among these schemes, Tessier's sequential extraction procedure is the most widely used method, which is initially developed for sediment analysis [12, 15]. In Tessier's method, heavy metals are classified as five fractions: exchangeable, bound to carbonate, bound to Fe-Mn oxides, bound to organic matter, and residual fractions [12]. The mobility, bioavailability, chemical behavior, and related eco-toxicity of heavy metals mainly depend on their specific speciation [5, 16–19]. Therefore, the combination of total concentration and speciation analysis of heavy metals in sediments can offer a realistic estimate of their actual environmental impact [3, 20–21].

In addition to the assessment of contamination levels and the bioavailability of heavy metals, it is also extremely important to determine the source of pollution. Pb isotopes can serve as an effective tool for distinguishing various sources of Pb because the Pb isotopic composition exhibits a natural variability among

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different sources, and the fractionation of Pb isotopes does not occur in industrial and environmental processes [22–26]. ^{206}Pb , ^{207}Pb , and ^{208}Pb are commonly used for identifying Pb pollution sources. Research has shown that Pb derived from anthropogenic sources usually has a lower $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio than natural Pb in sediments [1, 27–28]. Moreover, Pb in different fractions shows different Pb isotope ratios. Generally, the lowest $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio was observed in the exchangeable fraction, while the residual fraction showed the highest $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio [28]. This implies that Pb from anthropogenic sources is more prone to enrichment in non-residual fractions.

The Xiangjiang River, which traverses a distance of 817 km from its source in Xin'an of Guangxi Province to its confluence with the Yangtze River in Dongting Lake, is the largest river in Hunan Province and one of the major tributaries of the Yangtze River. The water of the Xiangjiang River is used for irrigation, domestic and industrial purposes. However, most of the ores for mining, mineral processing, and smelting of non-ferrous and rare metals in Hunan Province are located in the middle-downstream portion of the Xiangjiang River valley [29]. A long history of industrial activities in this area has led to the heavy metal contamination of sediments, especially in the vicinity of Hengyang and Zhuzhou [29]. Since the 1980s, research based on the total metal concentration and speciation of heavy metals in sediments from the Xiangjiang River has been conducted to assess the contamination levels and ecological risks [29–32]. However, most of previous studies were focused on specific tributaries or parts of the Xiangjiang River, and little information on the Pb isotopic composition of the sediments of the Xiangjiang River is available.

In the present work, the heavy metal concentration and speciation of sediments sampled along the Xiangjiang River in Hunan Province were investigated, and the Pb isotope compositions in different chemical fractions were determined. The main objectives of this work are to examine the contamination level of heavy metals, evaluate the mobility and bioavailability of heavy metals by sequential extraction, and investigate the possible sources of heavy metal contamination using Pb isotopic composition.

2 Materials and methods

2.1 Sediment sampling and pretreatment

Sediment samples were collected at 43 sites along the Xiangjiang River in January 2010 (Fig. 1). Surface sediment samples (0–15 cm) were collected using a grab sampler, placed in polyethylene plastic bottles, and labeled. To allow for further laboratory analysis, the

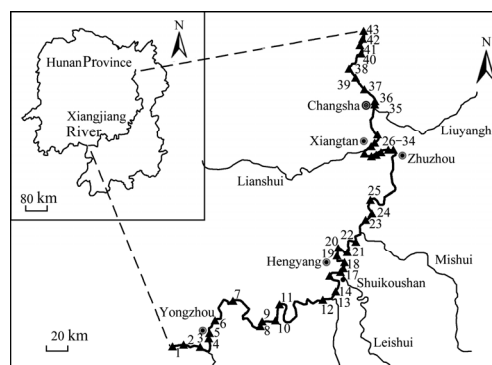


Fig. 1 Locations of sampling sites of sediments from Xiangjiang River

sediments were transported in an icebox and stored at $-20\text{ }^{\circ}\text{C}$. Samples for metal concentration analysis were all air dried and passed through a $63\text{ }\mu\text{m}$ sieve [17, 33]. In addition, the smelting flue gas dust, wastewater, and slag samples discharged by metallurgical and chemical plants in two heavily polluted areas (Zhuzhou and Hengyang) were collected to determine the sediment pollution source [34].

2.2 Sequential extraction

A five-step sequential extraction following the method of TESSIER et al [12] with little modification was conducted using 1 g of dried sediment. The extraction procedure is summarized as follows. 1) The exchangeable fraction was determined by adding 8 mL 1 mmol/L MgCl_2 solution ($\text{pH}=7$) and shaking for 1 h at $25\text{ }^{\circ}\text{C}$ with 200 r/min; 2) The carbonate fraction was determined by adding 8 mL of 1 mmol/L acetate buffer solution $\text{CH}_3\text{COOH}+\text{CH}_3\text{COONa}$ at $\text{pH}=5$ and shaking for 5 h at $25\text{ }^{\circ}\text{C}$ with 200 r/min; 3) The Fe-Mn oxides fraction was determined by adding 20 mL of 0.04 mmol/L $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% acetic acid solution (V/v) and shaking for 5 h at $96\text{ }^{\circ}\text{C}$ with 100 r/min; 4) The organic fraction was determined by adding 10 mL of 30% H_2O_2 and three drops of concentrated nitric acid and shaking for 2 h at $85\text{ }^{\circ}\text{C}$ with 100 r/min, adding an additional 5 mL of H_2O_2 and shaking for another 3 h, and then allowing the mixture to cool to room temperature before adding 10 mL of 0.5 mmol/L $\text{NH}_4\text{CH}_3\text{COOH}$ in a 20 mL acetic acid solution and shaking for an additional 30 min with 200 r/min; 5) The residual fraction was determined by adding 10 mL concentrated nitric acid, 6 mL HF, and 6 mL perchloric acid sequentially to the sediment and evaporating the mixture to near dryness on an electric hot plate. The total metal content was calculated by the sum of concentrations of five fractions.

2.3 Measurement of metal concentrations and quality control

The concentrations of Cr, Ni, Cu, Cd, Pb, and Zn

were analyzed by ICP-MS (Thermo Fisher XSeries II, Thermo Fisher Scientific). To preclude outside contamination, all the containers used in the experiments were soaked in a HNO₃ solution for 24 h and washed thoroughly with ultra-pure deionized water. All reagents used were guaranteed reagent grade.

An indirect examination of the reliability of metal concentrations determined by the sequential extraction procedure was made by working comparison of the sum of the concentrations found for the five fractions and the total metal concentration data using a certified reference material (GBW 08301, sediment of Xiangjiang River, National Institute of Metrology, China). Recoveries generally ranging from 80% to 120% were obtained, and mean recoveries were 91.1% for Cr, 103.7% for Ni, 109.6% for Cu, 96.1% for Cd, 84.6% for Pb, and 124.8% for Zn, and the results demonstrate the robustness of the sequential extraction procedure used in this work. Duplicate analysis also showed a good precision as the mean RSD was less than 10% for Cr, Ni, Cu, Cd, Pb, and Zn.

2.4 Pb isotope analysis

The solutions extracted by sequential extraction and acid digestion were also used to determine the Pb isotopic composition using ICP-MS (Thermo Fisher XSeries II, Thermo Fisher Scientific). To optimize the analytical performance, the solutions were diluted to a Pb mass concentration of approximately 10–50 µg/L using 2% HNO₃ (volume fraction) [35]. Repeated analysis (six times per sample) showed a good precision, and the RSD was less than 0.5%. A standard reference material (NIST SRM 981) was used for quality control and run between each of the six samples to ensure the accuracy of isotope measurement. Measurements were repeated when the difference between the measured and certified values exceeded 0.5%.

2.5 Contamination and bioavailability assessment

The potential ecological risk index (R_1) was used to assess the ecological risks of heavy metals in sediments [36]. R_1 was calculated using the following equations:

$$C_f^i = C_n^i / C_0^i \tag{1}$$

$$E_r^i = T_r^i \times C_f^i \tag{2}$$

$$R_1 = \sum_{i=1}^n E_r^i \tag{3}$$

where C_f^i is the single metal pollution index; C_n^i is the total content of metal i in the samples; C_0^i is the reference value for the metal i ; E_r^i is the single metal potential ecological risk index; T_r^i is the metal's toxic response factor, 1 for Zn, 2 for Cr, 5 for Cu, Ni and Pb,

10 for As, 30 for Cd, and 40 for Hg [36–37]; and R_1 is the potential ecological risk caused by the overall contamination. HAKANSON [36] distinguished five classes of E_r^i , and four classes of R_1 (Table 1).

Table 1 Pollution grades of potential ecological risk of heavy metals

E_r^i	Potential ecological risk	R_1	Ecological risk in environment
$E_r^i < 40$	Low risk	$R_1 < 150$	Low risk
$40 \leq E_r^i < 80$	Moderate risk	$150 \leq R_1 < 300$	Moderate risk
$80 \leq E_r^i < 160$	Considerable risk	$300 \leq R_1 < 600$	Considerable risk
$160 \leq E_r^i < 320$	High risk	$600 \leq R_1$	Very high risk
$320 \leq E_r^i$	Very high risk		

The mobility and bioavailability of heavy metals were assessed using the risk assessment code (RAC), which evaluates mobility and bioavailability by the percentage of heavy metals in exchangeable and carbonate fractions. Five grades of environmental risk were classified by RAC: no risk (less than 1%), low risk (1%–10%), medium risk (11%–30%), high risk (31%–50%) and very high risk (more than 50%) [5, 38].

2.6 Statistical analysis

All statistical analyses were conducted using SPSS 16.0 for Windows. A one-way ANOVA was employed to test differences among various data sets. The graphs were created with Microsoft Excel 2007.

3 Results and discussion

3.1 Total content of metals

The heavy metal concentrations in sediments collected from the Xiangjiang River are summarized in Table 2. The pollution index (PI) defined as the ratio of metals concentrations in sediments with corresponding background values is shown in Fig. 2. Compared with the samples collected from the highly polluted areas of the Xiangjiang River in previous studies (Table 2), lower concentrations of Cu, Cd, Pb, and Zn are observed in this work. The mean concentrations of metals are in the order of Zn>Pb>Cr>Ni>Cu>Cd (Table 2), while the PI values of metals are in the order of Cd>Zn>Cu>Pb>Cr>Ni (Fig. 2). Obviously, Cd had the highest contamination level. PI values for Cd at all sampling sites are greater than 1, and the mean PI value reaches 22.4. PI values for Cu, Pb, and Zn at most of the sampling sites are also greater than 1, and the mean PI values are 2.8, 2.8, and 5.3, respectively. Higher PI values for Cu, Cd, Pb, and Zn are generally found at sites near Zhuzhou and Hengyang (Fig. 1), where a lot of mining and smelting industries are located. Thus, the anthropogenic mining

and smelting activities along the Xiangjiang River are probably responsible for the enrichment of these four metals as reported by GUO et al [29]. Although Cr and Ni show higher concentrations, their mean PI values are 1.2 and 1.0, respectively. PI values for Cr and Ni at sites near Hengyang and Zhouzhou (Fig. 1) also show no peaks as Cu, Cd, Pb and Zn. This suggests little anthropogenic input of Cr and Ni to sediments.

Correlation analysis shows significant correlation between Cu, Cd, Pb, and Zn ($p < 0.01$), between Cr and Ni ($p < 0.05$), and between Cr and Zn ($p < 0.05$) (Table 3). Cr is not significantly correlated with Cu, Cd, or Pb, and

Ni is not significantly correlated with Cu, Cd, Pb, or Zn (Table 3). Significant correlation among metals indicates their possible similar sources [40]. Thus, Cu, Cd, Pb, and Zn may have similar sources different from Cr and Ni. Combined with the PI values of Cu, Cd, Pb, and Zn discussed above, they probably originate from similar anthropogenic sources related to mining and smelting activities. Contrarily, Cr and Ni are probably from similar natural sources. Cd is usually associated with Pb-Zn ore and Cu ore, and thus is released into the environment together with Cu, Pb, and Zn during mining and smelting processes [3].

Table 2 Heavy metal concentrations in sediments (mg/kg)

Data	Value/Range	Cr	Ni	Cu	Cd	Pb	Zn
This work	Mean \pm SD	65.7 \pm 18.3	39.5 \pm 13.5	60.9 \pm 35.6	13.4 \pm 10.8	111.8 \pm 59.0	390.3 \pm 253.4
	Range	27.1–109.9	18.0–65.1	19.3–187.2	0.96–55.1	33.0–311.8	42.1–1207.7
Ref. [30]	Mean	—	—	100	7.8	290	660
	Range	—	—	9.2–1500	0.17–78	11–2400	7.9–7500
Ref. [31]	Range	—	—	9.2–720	1.3–78.4	20–2300	12.2–6100
Ref. [39]		54	40	22	0.6	40	73

SD means standard deviation.

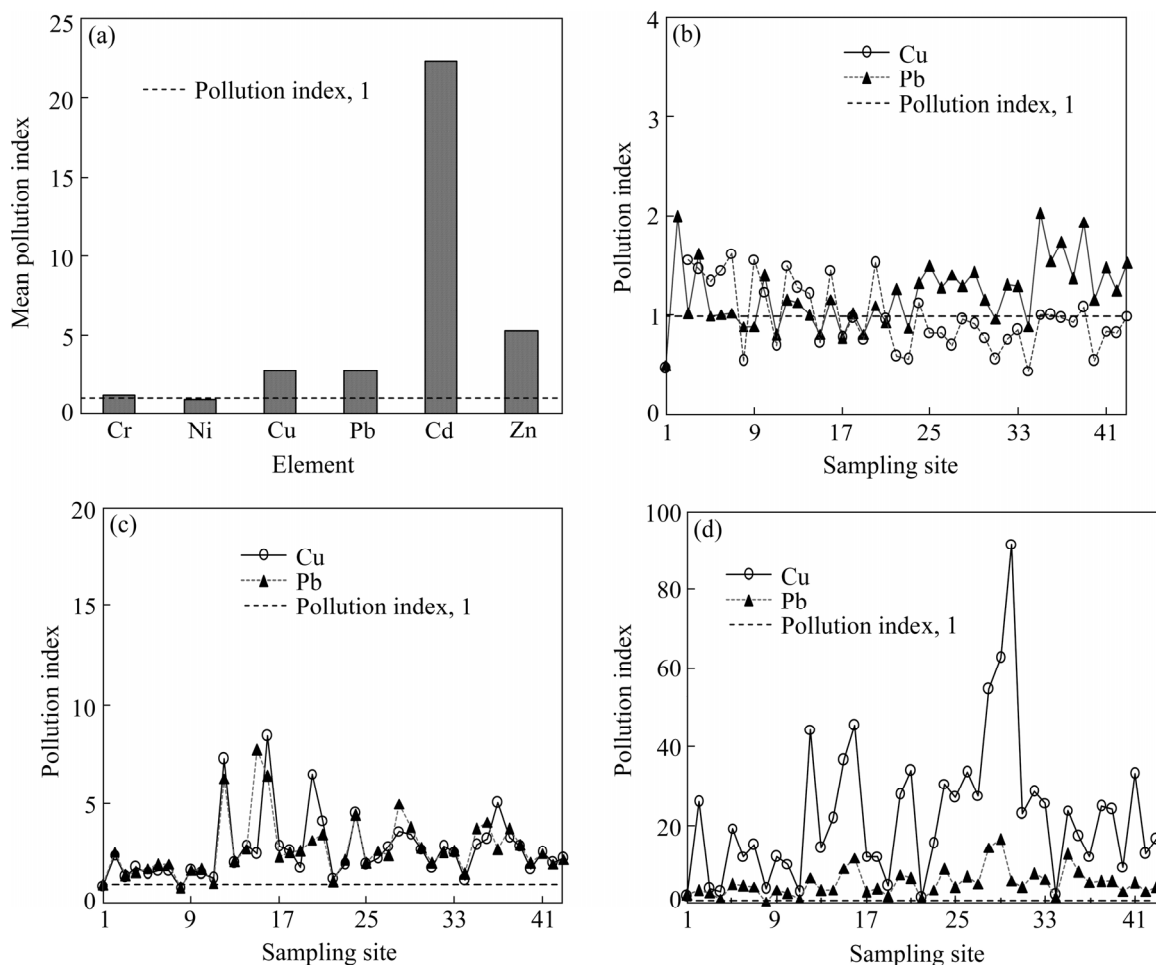


Fig. 2 Pollution index (PI) of metals in sediment from sampling sites: (a) Mean pollution index; (b) Pollution indices for Cr and Ni; (c) Pollution indices for Cu and Pb; (d) Pollution indices for Cd and Zn

Table 3 Correlation matrix of heavy metals in sediments

Element	Cr	Ni	Cu	Cd	Pb	Zn
Cr	1.000					
Ni	0.380*	1.000				
Cu	0.209	0.208	1.000			
Cd	0.202	0.060	0.503**	1.000		
Pb	0.145	0.108	0.724**	0.597**	1.000	
Zn	0.332*	0.035	0.576**	0.706**	0.724**	1.000

* Significant at $p < 0.05$ (two-tailed); ** Significant at $p < 0.01$ (two-tailed).

The ecological risk assessment was conducted using Eqs. (1)–(3) listed and based on the sediment background values in Table 2. The mean values and ranges of E_r^i for Cr, Ni, Cu, Cd, Pb, Zn are 2.4 (1.0–4.1), 4.9 (2.3–8.1), 13.8 (4.4–42.5), 671.2 (48.0–2756.6), 14.0 (4.1–39.0), 5.3 (0.6–16.5), respectively. The mean values of E_r^i are in the order of $Cd > Pb > Cu > Zn > Ni > Cr$. Cd has the highest potential ecological risk (Fig. 3). Sites rated as very high risk account for nearly 80% of the sites sampled, and the remaining sites are at least in moderate risk. Contrarily, the other metals show low potential ecological risk, although concentrations of Cu, Pb, and Zn are also higher than corresponding background values. The present results suggest that the risk posed by Cd should be of great concern.

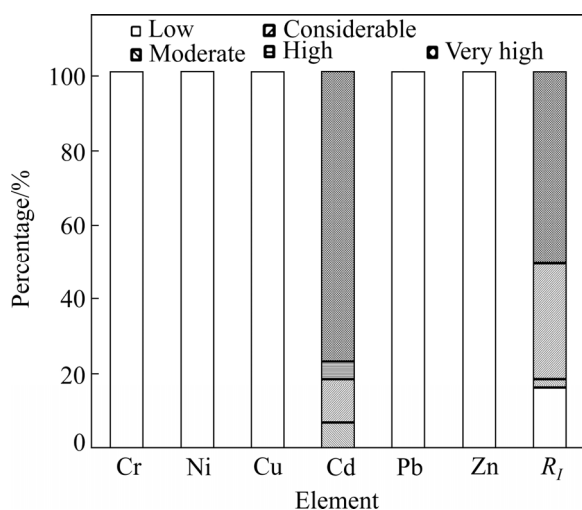


Fig. 3 Percentage of sampling sites in different potential ecological risks based on results of E_r^i (Cr, Ni, Cu, Cd, Pb, Zn) and R_1 .

The risk factor R_1 was proposed by HAKANSON [36] based on eight metals (As, Hg, Cr, Ni, Cu, Cd, Pb, and Zn). In this work, As and Hg were excluded. Based on the background values of these metals, the ecological risk index R_1 values are calculated. The mean value and range of R_1 are 711.6 and (67.2–2797.1). The percentages of sampling sites that are classified as low risk, moderate risk, considerable risk, high risk, and very high risk are

16.3%, 2.3%, 30.2%, 0%, and 51.2%, respectively (Fig. 3). This indicates that most of the sediments from the Xiangjiang River show considerable or very high potential ecological risk. Among the metals considered, Cd which contributes largely (~90%) to the RI in all sampling sites due to its high E_r^i is the main pollution metal in sediments of the Xiangjiang River.

3.2 Metal speciation

Figure 4 summarizes the fractional distribution of heavy metals in all sampling sites. The residual fraction of Cr (61.8%–90.5%) is the most dominant fraction found in the sediments of all sampling sites, the Fe-Mn oxides fraction of Cr (4.3%–19.5%) is the second highest, but the exchangeable and carbonate fractions of Cr account for only a very small proportion. The residual (41.6%–85.9%) and Fe-Mn oxides (7.8%–44.9%) fractions are also the most dominant for Ni. Similar Cr fractionation results have been reported by ALBA et al [41] and DAVUTLUOGLU et al [7]. The fact that Cr and Ni are largely bound to the inert fraction also indicates their natural sources as shown by their concentrations and correlation analysis (Tables 2 and 3).

For Cu, Fe-Mn oxides and organic fractions, which are 9.7%–47.0% and 16.2%–52.0%, respectively, are the most dominant fractions along with the residual fraction (13.1%–65.5%). A large proportion of Cu is found in the organic fraction, which is a result of Cu’s ability to form stable organic complexes [42]. This agrees with the results of previous studies that show a high proportion of organic Cu in sediments [17, 31–32].

Cd is mainly bound to non-residual fractions, mainly to the exchangeable (7.2%–54.4%), carbonate (7.6%–58.1%) and Fe-Mn oxides fractions (21.3%–62.3%), but rarely to the organic fraction (1.0%–28.6%). The fraction analysis of sediments from the Xiangjiang River carried out by other researchers also shows that a high proportion of Cd is in the carbonate (9%–33%) or Fe-Mn oxides fractions (15%–65%) [30–31]. Cd in sediments of the Yamuna River and the Yangtze River are also primarily bound with the exchangeable and carbonate fractions [3, 5]. The high proportion of carbonate-bound Cd in sediments from the Xiangjiang River may be ascribed to the fact that carbonates are common in this area and that the similarity of the ionic radii of Ca and Cd favors the co-precipitation of Cd carbonate and its incorporation into the calcite lattice [21, 31]. Pb and Zn are primarily bound to Fe-Mn oxides in proportions of 31.5%–64.0% for Pb and 17.5%–91.0% for Zn. The residual fraction of Pb (7.4%–35.9%) and Zn (10.9%–75.2%) also accounts for a large proportion. In addition, a moderate amount of Pb (8.7%–27.6%) exists in the organic fraction. ZHANG et al [32] also found that Pb and Zn are mostly found in

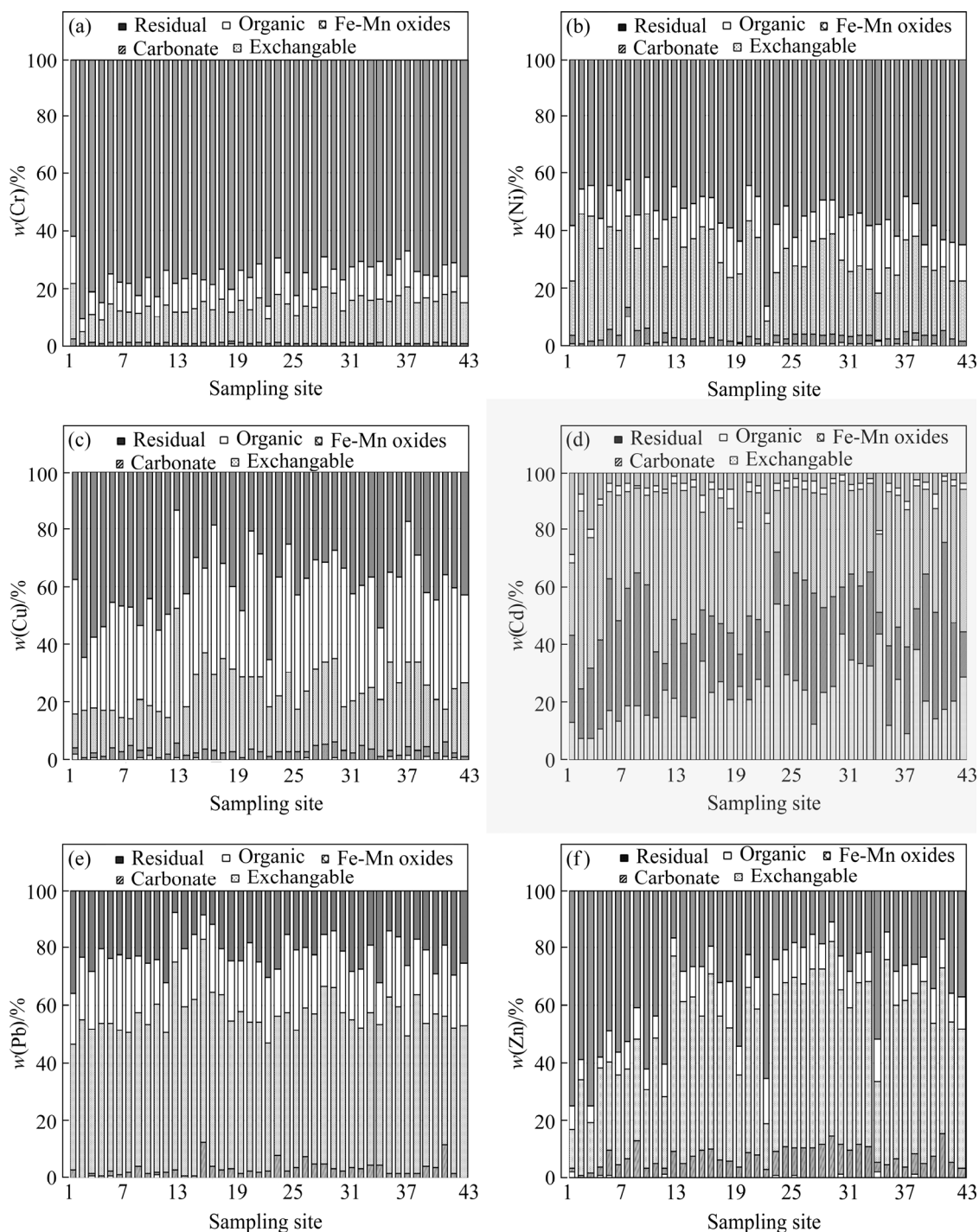


Fig. 4 Fractionation of trace metals in sediments from Xiangjiang River into five operationally-defined fractions in 43 sampling sites: (a) Cr; (b) Ni; (c) Cu; (d) Cd; (e) Pb; (f) Zn

the Fe-Mn oxides fraction in sediments from the Xiangjiang River. Fe-Mn oxides have high scavenging efficiencies for heavy metals and thus become sinks for heavy metals [5, 43]. Consequently, in addition to Pb and Zn, higher Cr, Ni, Cu, and Cd concentrations are also found in the Fe-Mn oxides fraction.

Heavy metals that exist in different fractions will show different bioavailability. The residual fraction, which is inert, is strongly bound to silicates and can only

be released under very harsh conditions [11]. Heavy metals in the Fe-Mn oxides and organic fractions are subjected to release when the redox potential changes, whereas the exchangeable and carbonate fractions are the most liable to release into the environment [11]. Thus, the RAC which assesses the mobility and bioavailability of heavy metals by applying a scale to the percentage of metals in the exchangeable and carbonate fraction can provide further evaluation.

The values of RAC for Cr, Ni, Cu, Cd, Pb, and Zn are (1.0±0.3)%, (3.3±2.1)%, (3.1±1.4)%, (51.3±11.2)%, (3.1±2.5)%, and (7.2±3.5)%, respectively (Fig. 5). Generally, the RAC of Cr is less than 1%, indicating that Cr presents no risk, and the RACs of Ni, Cu, Cd, Pb, and Zn are in the range of 1%–10%, indicating their low risk. For Cd, 97.7% of the sampling sites are classified as high or very high risk according to the RAC. In another words, the bioavailability of metals following the order: Cd>Pb≈Zn≈Cu≈Ni>Cr($p<0.05$). A higher risk of Cd was also found in other heavy-metal polluted rivers [5, 21]. Similar results were found by the ecological risk assessment and RAC.

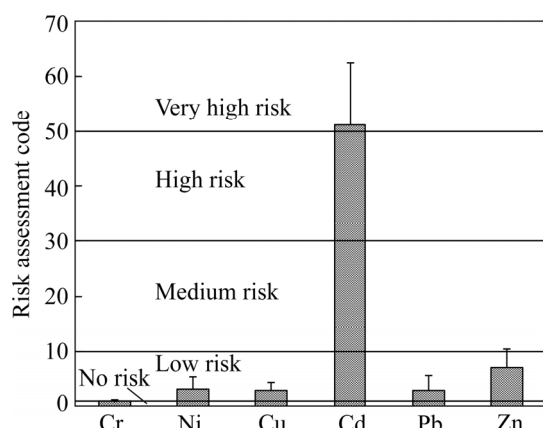


Fig. 5 Risk assessment code (RAC) of heavy metals in sediments from Xiangjiang River

3.3 Pb isotope

3.3.1 Identification of sources

Table 4 shows the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratios in various fractions to be in the order of exchangeable (1.163±0.012)<carbonate (1.179±0.005)≈Fe-Mn oxides (1.181±0.006)≈organic (1.182±0.006)<residual (1.208±0.017) ($p<0.05$). Moreover, the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratios in the exchangeable fraction (1.163±0.012) is similar with the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratios in the wastewater, dust,

and slag released by mining and smelting plants along the Xiangjiang River (1.162±0.020) (Table 4). It was reported that anthropogenic Pb is usually characterized by a low $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio (<1.2), while geogenic background Pb generally presents a higher $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio (about 1.2) [28, 44]. Thus, in this work, Pb found in the exchangeable fraction may primarily come from anthropogenic sources. However, the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio in the residual fraction (about 1.2) indicates a natural source. This is supported by SUN et al [44] who found that the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratios of uncontaminated sediments collected at depth of 50–100 cm from the Xiangjiang River is approximately 1.2 (1.198±0.002). The $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratios of the carbonate (1.179±0.005), Fe-Mn oxides (1.181±0.006), and organic fractions (1.182±0.006) are between those of the exchangeable and residual fractions, and no significant difference ($p<0.05$) among the three fractions was observed. This result is in agreement with the study conducted by LI et al [1], and explained by Pb in the three fractions are from the similar Pb sources of both natural and anthropogenic sources. SUN et al [44] showed that the mean value of the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio of total Pb content in polluted sediments collected at depth of 0–50 cm from the Xiangjiang River is 1.181, which is similar with the mean value of the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio of the three fractions in present work (Table 4) [44]. This confirms the impact of anthropogenic Pb on the three fractions.

The correlation between Pb content and the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio in various fractions is shown in Fig. 6. An evident trend of decreasing $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio with increasing Pb content is observed for Fe-Mn oxides and organic fractions, which is ascribed to the accumulation of anthropogenic Pb with lower $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratios. This indicates the input of anthropogenic Pb to these two fractions. However, the low contents of exchangeable and carbonate Pb shown in

Table 4 Pb isotopic composition in sediments

Type	$w(^{206}\text{Pb})/w(^{207}\text{Pb})$		$w(^{208}\text{Pb})/w(^{206}\text{Pb})$	
	Mean ± SD ^a	Range	Mean ± SD	Range
Exchangeable	1.163 ± 0.012	1.148–1.206	2.099 ± 0.022	2.025–2.129
Carbonate	1.179 ± 0.005	1.166–1.192	2.080 ± 0.008	2.062–2.100
Fe-Mn oxides	1.181 ± 0.006	1.169–1.196	2.083 ± 0.010	2.056–2.098
Organic	1.182 ± 0.006	1.166–1.193	2.083 ± 0.011	2.057–2.102
Residual	1.208 ± 0.017	1.185–1.273	2.066 ± 0.020	2.013–2.102
Waste water, dust and slag ^b	1.162 ± 0.020	1.129–1.180	2.122 ± 0.023	2.099–2.160
XJ (0–50) ^c	1.181			
XJ (50–100) ^c	1.198 ± 0.02			

^a SD means standard deviation; ^b Wastewater, dust, and slag released by metallurgical and chemical plants along the Xiangjiang River [34]; ^c XJ (0–50) sediments collected at depth of 0–50 cm from the Xiangjiang River, XJ (50–100) sediments collected at depth of 50–100 cm from the Xiangjiang River [44].

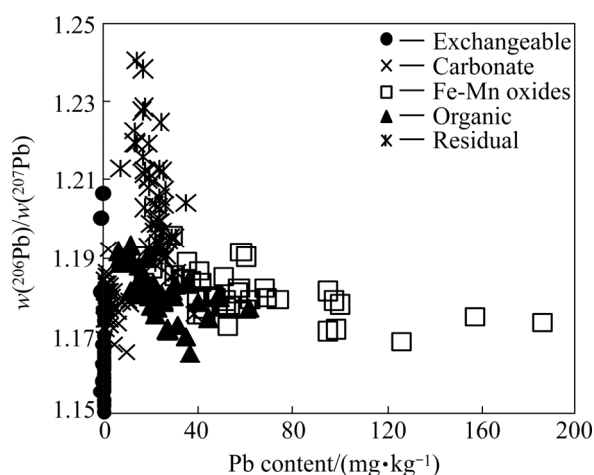


Fig. 6 Relationship between Pb content and $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio in various fractions

Fig. 4 makes this trend inconspicuous, yet lower $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratios were also found for exchangeable and carbonate fractions (Table 4). Residual Pb shows no such trend because of its geogenic origin. SUN et al [44] and WONG et al [45] also found the Pb content and the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio in total content from sediments suffering heavy metal pollution showed the same trend.

The isotopic composition of Pb, expressed as $w(^{208}\text{Pb})/w(^{206}\text{Pb})$ vs. $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratios, is shown in Fig. 7. The linear relationship of the two ratios can be observed, and which was also found in other studies and indicates a binary mixing source of Pb [28, 44–47]. As demonstrated above, the residual fraction characterized by high $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ and low $w(^{208}\text{Pb})/w(^{206}\text{Pb})$ ratios is representative of the natural source of Pb (Fig. 7). While, wastewater, dust, and slag (Table 4) characterized by low $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ and high $w(^{208}\text{Pb})/w(^{206}\text{Pb})$ ratios are the major anthropogenic sources of Pb in sediments (Fig. 7).

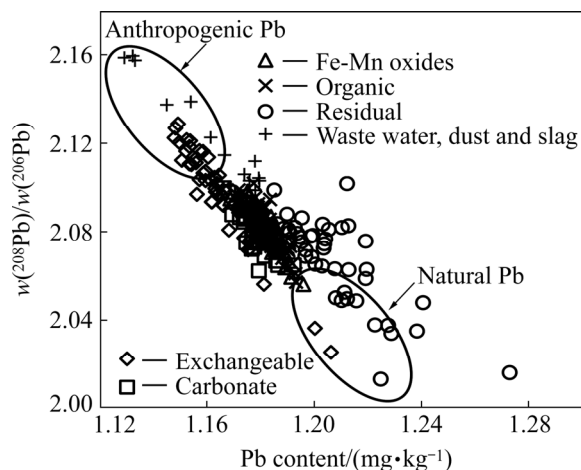


Fig. 7 Relationship between $w(^{208}\text{Pb})/w(^{206}\text{Pb})$ and $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratios in various fractions, and waste water, dust and slag

3.3.2 Source apportionment

The percentage of anthropogenic Pb can be calculated by

$$\text{Pb}_{\text{AC}} = \frac{w(^{206}\text{Pb})/w(^{207}\text{Pb})_{\text{MC}} - w(^{206}\text{Pb})/w(^{206}\text{Pb})/w(^{207}\text{Pb})_{\text{AC}} - w(^{206}\text{Pb})/w(^{207}\text{Pb})_{\text{BC}}}{w(^{206}\text{Pb})/w(^{207}\text{Pb})_{\text{BC}}} \quad (4)$$

where AC is the anthropogenic component, MC is the measured component, and BC is the background component [46, 48].

The mean value of the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ (1.162) ratio of the wastewater, dust, and slag released by mining and smelting plants (Table 4) is assumed to be the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ of the main anthropogenic Pb. The $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ of the residual fraction in sediments is regarded as the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ of background Pb. On the basis of the assumption that two main sources exist, the percentages of anthropogenic Pb in the exchangeable, carbonate, Fe-Mn oxides, and organic fractions calculated by Eq. (4) are $(91.3 \pm 16.7)\%$, $(61.1 \pm 13.9)\%$, $(57.4 \pm 11.1)\%$, and $(55.5 \pm 11.2)\%$, respectively. This confirms exchangeable Pb is primarily from anthropogenic sources. Moreover, for the sediments from the Xiangjiang River, the carbonate, Fe-Mn oxides, and organic fractions are also seriously polluted. According to SUN et al [34], the mean value of the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ of total Pb content in the Xiangjiang River sediments is 1.181. Thus, the contribution of anthropogenic Pb to total Pb in sediment calculated by Eq. (4) is $(54.0 \pm 14.9)\%$. This suggests that more than half of the Pb in sediments from the sampled sites comes from pollution. The percentage of anthropogenic Pb can also be obtained by the total Pb concentration and the background Pb concentration found in Table 2, and the results show that anthropogenic Pb accounts for $(55.5 \pm 21.1)\%$ of the Pb found in surface sediments, which is similar to the results obtained by $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratios. This confirms the reasonability of using mean values of the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio found for the wastewater, dust and slag released by mining and smelting plants to represent the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratio of anthropogenic Pb.

4 Conclusions

Enrichment of Cu, Cd, Pb, and Zn is found in the sediments from the Xiangjiang River. Ecological risk assessment shows that Cd exhibits very high ecological risk, while other heavy metals only show low ecological risk. Sequential extraction reveals that the residual and Fe-Mn oxides fractions yield the highest percentages of Cr and Ni, the Fe-Mn oxides, organic and residual fractions yield the highest percentage of Cu, the non-residual fractions, mainly the exchangeable, carbonate,

and Fe-Mn oxides fractions, yield the highest percentages of Cd, and the Fe-Mn oxides fraction yields the highest percentages of Pb and Zn. Correlation analysis reveals that Cr and Ni are mainly derived from natural sources, while Cu, Cd, Pb, and Zn are mainly derived from anthropogenic sources. The Pb isotope analysis shows that the $w(^{206}\text{Pb})/w(^{207}\text{Pb})$ ratios in various fractions are in the order of exchangeable (1.163 ± 0.012) < carbonate (1.179 ± 0.005) \approx Fe-Mn oxides (1.181 ± 0.006) \approx organic (1.182 ± 0.006) < residual (1.208 ± 0.017) ($p < 0.05$). Wastewater, dust, and slag from mining and smelting areas in the Xiangjiang valley are the primary anthropogenic sources of Pb, while residual Pb represents the natural sources of Pb. The percentages of anthropogenic Pb exchangeable, carbonate, Fe-Mn oxides, and organic fractions are (91.3 \pm 16.7)%, (61.1 \pm 13.9)%, (57.4 \pm 11.1)%, and (55.5 \pm 11.2)%, respectively. This confirms that the significant accumulation of anthropogenic Pb in the exchangeable fraction, and the serious pollution in carbonate, Fe-Mn oxides, and organic fractions.

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