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# Heavy metals migration in soil in tailing dam region of Shuikoushan, Hunan Province, China

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## Abstract

The nonferrous mining industry in China has been exploiting rich domestic mineral resources in order to sustain rapidly economic and social development. The paper chooses the tailing dam region as the research object in the Shuikoushan, and researches the distribution of Pb, Zn, Cu, Cd, As, Cr, which reveals heavy metal migration regularities in layers from new and old tailing dam region. In addition, this article focuses on making the research of Potential Ecological Risk Index appraisal to the heavy metal contamination level. The results showed that the concentrations of heavy metals in old tailing dam region were much higher than those of in the new tailing dam region. As well, the concentrations of most heavy metal reduced progressively with the soil depth increasing for the new tailing dam region, while the change tendency was inversely for the old one. Potential ecological risk index showed that the potential ecological risks were at low and low to moderate level in tailing dam region.

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Keywords: Tailing dam; Heavy metals; Shuikoushan; Ecological risk index; heavy metals migration.

# 1. Introduction

The nonferrous mining industry in China has been exploiting rich domestic mineral resources in order to sustain rapidly economic and social development. However, the increase of heavy metals in the environment caused by mining activities has added to environmental deterioration in recent decades 1. Hunan, a province in south of China, is located in the center area of acid deposition. Meanwhile, Hunan is

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also called as "the town of nonferrous metals in China", meaning that there are many large deposits of heavy metals in Hunan2.

This study was conducted in Shuikoushan in Changning County, Hunan Province in central south China. There are many Pb/Zn mines, smelters and tailing dams locating along the southern shore of the Xiangjiang River, the largest river in Hunan Province. Mining and smelting activities were initiated early in 1889 and have been developed rapidly since the 1950s. The new tailing dam was built in 1980s and the old tailing dam was closed in 2000s. Several million tonnes of tailings have been piled up. These wastes, which contain high contents of heavy metals such as Cd, Pb, Zn, Cu, and low concentrations of N, P, and organic matter have caused severe environmental pollution in the mining area3. Kangjiaxi River, a branch of the Xiangjiang River, flows between new and old tailing dam. The area is within the sub-tropic zone, with average annual temperature of 18.7°C, annual rainfall of 1442 mm, and north-western prevailing winds. The land is relatively flat and slightly hilly. Most of the lands are cultivated with rice from June to October every year and some lands near the mines, smelters and tailing dams were left uncultivated because of the low.

Heavy metals can enter the soils in three primary ways: by wastewater of mining, exhaust gas and waste residue of smelting and leaching of tailing dam5. At present, most studies on mainly focused on mining and smelting areas and lacking of environment around tailing in Shuikoushan. The heavy metal pollutants should be paid more attention, because the contaminations have a serious harm to humans and animals. The purpose of this study is to investigate the heavy metal contents of surface soils in the area of Shuikoushan. Furthermore, ecological risk index (RI) is used to assess the heavy metals accumulations and compared analyze the migration of heavy metals in soils around the new and old tailing dam.

### 2. Materials and methods

A total of thirteen points were selected to collect soils from Shuikoushan. Among those points, S1, S2, S3 and S4 were in the old tailing dam, namely, closed tailing dam and the others were in the area of a current tailing dam. Furthermore, as shown in Figure 1, S5-8 were collected from the soil surface (0-20cm), S1-4 and S9-13 were collected from the soil profile divided into three layers, 0-20cm 20-60cm 60-100cm, respectively.



Fig.1 Map of sampling areas (the "." represents the location of the sampling site)

As soon as the field work was finished, soil samples were carefully shipped to laboratory. Then the samples were dried at 105 °C and grounded to powers, sieved through a 100 mesh sieve and kept in a pre-

cleaned container for further use. Samples were digested with a mixture of HNO<sub>3</sub>–HF–HClO<sub>4</sub>. Then, the contents of Pb, Zn, Cu, Cd and Cr were analyzed by FAAS (Flame Atomic absorption spectroscopy, AA7000F/AAC) as well as by AFS (Atomic fluorescence spectroscopy, AFS-3100).

## 3. Results and discussion

pH was from 3.99 to 6.86. To facilitate analysis data, the sampling site was indicated by Sij. i was sampling number, j was layers. The number of i was from 1 to 13, and j was 1, 2 and 3.

 $X_{new,j}$  is the average concentration of the heavy metal in S9-S13 in the j layer.

 $\overline{X}_{old,j}$  is the average concentration of the heavy metal in S1-S4 in the j layer.

$$\overline{X}_{new,1} = \frac{1}{5} \sum_{i=9}^{13} S_{i,1} ; \overline{X}_{new,2} = \frac{1}{5} \sum_{i=9}^{13} S_{i,2} ; \overline{X}_{new,3} = \frac{1}{5} \sum_{i=9}^{13} S_{i,3} ; \overline{X}_{old,1} = \frac{1}{5} \sum_{i=1}^{4} S_{i,1} ; \overline{X}_{old,2} = \frac{1}{5} \sum_{i=1}^{4} S_{i,2} ; \overline{X}_{old,3} = \frac{1}{5} \sum_{i=1}^{4} S_{i,3} ; \overline{X}_{old,3} = \frac{1}{5} \sum_{i=1}^{4} S_{i,3} ; \overline{X}_{old,2} = \frac{1}{5} \sum_{i=1}^{4} S_{i,2} ; \overline{X}_{old,3} = \frac{1}{5} \sum_{i=1}^{4} S_{i,3} ; \overline{X}_{old,3} = \frac$$





Fig.2 The average concentrations of Cu in soil from different layers layers

Fig.3 The average concentrations of Zn in soil from different



Fig. 4 The average concentrations of Pb in soil from different layers different layers



Fig.5 The average concentrations of Cd in soil from





Fig.6 The average concentrations of Cr in soil from different layers different layers

Fig.7 The average concentrations of As in soil from

Heavy metal concentrations in the surface soil of Shuikoushan (mg/kg) ( $n = 39$ )												
		Raw	v data	Reference value	Background value of							
	Mean	Min	Max	SD	iterenete value	Hunan Province						
Cu	44.87	17.5	94.4	33.63	400	27.3						
Zn	739.35	93.5	1651	991.70	500	94.4						
Pb	209.90	20.7	801	228.89	500	29.7						
Cd	1.90	0.24	4.56	2.06	1	0.125						
Cr	89.51	58.8	138	22.99	300	71.4						
As	13.90	11.8	16.4	1.46	30	15.7						

Table 1 Heavy metal concentrations in the surface soil of Shuikoushan (mg/kg) (n =39)

Reference value: class III value of the Environmental Quality Standard for Soils in China (GB15618-1995)

A. The compared analysis of the average concentrations of heavy metals in soil in tailing dam

As shown in Table 1, soils in Shuikoushan have been greatly contaminated by Cd and Zn, with the average concentrations of the two elements all exceeding Class III of the Environmental Quality Standard for Soils in China (GB 15618-1995). Except for As, soils were also found to be contaminated by Cu, Pb, Zn, Cd and Cr, and the average concentrations of these five elements are all exceeding the background value of Hunan Province.

B. The compared analysis of heavy metals in soil in new and old tailing dam

The concentration curves of heavy metals in soil in new and old tailing dam region are shown from in Figure 2 to 7. The results showed that the concentrations of Cu in every layer in old tailing dam region were higher than that of in the new tailing dam region. Furthermore, the concentrations of other heavy metals such as Zn, Pb, Cd, Cr and As in every layer in the old tailing dam region were higher than that of in the new one too.

The conclusion is that the concentrations of heavy metals in old tailing dam region were higher than the ones of in the new tailing dam region.

C. The contents of heavy metals in the soil profile of new and old tailing dam region.

In case of the new tailings surrounding soil profile, the concentrations of Cu reduced gradually with the soil depth increasing. In contrast, the concentrations of Cu increased gradually with the soil depth increasing for old tailings surrounding soil.

The same change trend was proposed for Zn.

For the Pb, the concentration of Pb on the surface of soil was the highest whatever this metal in the new or old tailing dam surrounding was.

The elements of Cd and Cr exhibited the similar variation tendency with the Cu, namely, the concentrations of Cd and Cr reduced gradually with the soil depth increasing in new tailing surrounding. While the concentrations of Cd and Cr increased gradually with the soil depth increasing for old tailings surrounding soil.

As shown in Figure 7, it can conclude that the change of As is not obvious. This may be because: the element of As is easily to be adsorbed over the surface of soil clay.

In case of the new tailings surrounding soil, the concentrations of most kinds of heavy metal gradually reduced with the soil depth increasing. While the concentrations of most heavy metals increased gradually with the soil depth increasing for old tailings surrounding soil. This may possibly be due to continue a long time with a history of more than 100 years for the old tailing pond. The heavy metals are difficult to transfer in neutral soil6. The migration of heavy metals would be improved because the soil in the sampling sites area is acidic, which results in the concentrations of heavy metals in the bottom layer being higher than on the surface for the old tailings area.

D. Potential ecological hazard index

The formulas are as follows 7: Single heavy metal contamination factor:  $C_f^i = C^i / C_n^i$ , where,  $C_f^i$  is

contamination factor of heavy metal i;  $C^i$  is the measured concentration of heavy metal i;  $C_n^i$  is the assessment reference value. Potential ecological hazard coefficient of heavy metal i in a certain area:  $E_r^i = T_r^i \times C_f^i$ , where  $E_r^i$  is the potential ecological hazard coefficient of metal i;  $T_r^i$  is the toxic level of heavy metals and the organism's sensitivity towards heavy metals. The potential ecological hazard index of diverse heavy metals RI equals the total sum of all heavy metals ecological hazard index 8, the formula is as follows:  $RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \times C_f^i = \sum_{i=1}^{n} T_r^i \times C_r^i / C_n^i$ ,  $E_r^i < 40$ ,  $40 \le E_r^i < 80$ ,  $80 \le E_r^i < 160$ ,  $160 \le E_r^i < 320$ , state low, low to moderate, high and extremely high ecological risks. RI<150,  $150 \le RI < 300$ ,  $300 \le RI < 600$ , RI $\ge 600$  state low, low to moderate, high and extremely high ecological risks.

Sampling points			The poter	ntial ecolog	Hazard index	classification			
		Cu	Zn	Pb	Cd	Cr	As	KI	
	S5	2.87	0.67	3.25	15.6	2.73	8.73	33.86	low
New	S6	1.75	0.53	1.48	27	1.68	8.73	41.18	low
tailing	S7	7.32	4.95	28.29	76.2	1.64	7.87	126.26	low
dam	S8	4.3	4.54	35.36	136.8	1.61	8.6	191.21	low to moderate
	S9	3.63	1.11	8.21	13.5	1.42	9.93	37.81	low
Old tailing dam	S1	5.1	4.96	18.14	48.9	2.42	10.53	90.06	low
	S2	2.6	3.6	13.07	31.2	1.31	10.73	62.51	low
	S3	9.44	6.11	57.21	34.5	1.83	10.93	120.03	low
	S4	5.17	9.43	15.5	133.2	3.07	10.33	176.8	low to moderate

Table 2. Potential ecological hazard values in Shuikoushan

As shown in Table 2, from the single heavy metal contamination factor, the  $E_r^i$  of Cd in S4, S8 and S1, S7 of old and new tailing dam section are more than 80 and 40, which are high and low to moderate, respectively. Then the  $E_r^i$  of Pb in S3 was more than 40, which was low to moderate. The other metals in anywhere were all in low level. And from the results of the diverse heavy metal contamination factor RI, the heavy metals in S4 and S8 were low to moderate, the other points were low to ecological risks.

#### 4. Conclusions

In this paper, a series of data of concentrations of heavy metals was obtained and their performances were shown. The soils in Shuikoushan have been greatly contaminated by Cd, Zn, Cu, Pb and Cr, and the average concentrations of the Cd and Zn exceed Class III of the Environmental Quality Standard for Soils in China and the average concentrations of these five elements are exceeding the background value of Hunan Province. The results illustrated that the concentrations of heavy metals in old tailing dam region were higher than in new tailing dam region. As well, the concentrations of most heavy metal reduced progressively with the soil depth increasing for the new tailing dam region, while the change tendency was inversely for the old one. Meanwhile, the potential ecological risk index indicated that the potential ecological risks were at low and low to moderate level in tailing dam region.

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