Study on distribution characteristics of chromium and nickel in root soils around a typical abandoned alunite mining area

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Abstract. The exploitation of alunite resources results in the exposure of heavy metals to the surface surrounding, enrichment in soil and potential health risks to human beings. This study investigated the heavy metal pollution of root soils in a mining district surrounding a typical abandoned alunite mining area in Anhui province of China. Up to 10 root soil samples were collected in 20 sampling sites, and the concentration of Cr and Ni were determined. The results show that the root soils contained acceptable levels of Cr and Ni occurring in the ranges of 46.2-503.5 and 12.8-44 mg/kg, respectively. According to the National Soil Environment Quality Standards, few samples had Cr and Ni contents exceeding the risk screening values. However, due to the regional differences of background values, the geoaccumulation indices of Cr indicate slightly to extremely contaminated. Based on the calculation of potential ecological risk index, all the root samples were considered as low health risk level. These findings indicate the possible need for deeply and comprehensively investigation of heavy metals at alunite ore mines.

1 Introduction

Heavy metal pollution has been considered as one of the most important contaminations in soils. There are several routes which can accelerate the enrichment of heavy metals contents, included natural processes and anthropogenic activities ^[1]. Furthermore, heavy metals released from mining activities generally can be transported to soils surrounding, accumulated in plants and animals, and finally affected human health through food chain ^[2]. These issues would be clearly magnified if mines were abandoned without any management measure.

Alunite mining activities in Lujiang County, Anhui Province, were actively developed from the early twentieth century, but all of the mines had been closed gradually until the beginning of this century due to development policies and the exhaustion of alunite reserves. The rock structure was slightly destroyed with fracture network increasing, while a large amount of accumulated slag would cause serious harm to the surrounding environment. Thus, all of these changes could indirectly enhance the occurrence probability of secondary geological disasters in rainfall season, such as slope collapse, landslide and debris flow.

Compared with mining activities, the exploitation of alunite resources could more easily generate acid-mine drainage (AMD), based on the ionization of alunite ore and the oxidation of accompanying pyrite ^[3]. This feature further facilitates the soil heavy metal pollution in the alunite mining area.

In this study, contamination level and risk assessment of Cr and Ni in a typical abandoned alunite mine were

investigated. Based on the research results, remediation strategies for the studied mine were also provided.

2 Materials and methods

2.1. Sampling and analysis

Dominant plant and corresponding root soil samples were collected around the abandoned alunite mine (Fig. 1). About 15 varieties of local dominant plants in 20 sampling sites were taken, and carefully washed with deionized water to remove soil particles or dust adhered to the plant surface. The whole plant collection method was adopted, while 3 to 5 samples for each plant were randomly selected. Samples were then air-dried at 70 °C for 72 h. The dry samples were crushed and digested with a mixed solution (HNO₃:H₂O₂=8:2) for subsequent analyzation.

The corresponding soil samples were also collected by plum blossom method. After being naturally air-dried and making sure that debris, animal and plant residues and other impurities had been removed, soil samples were sieved through a 200-mesh nylon sieve. In order to determine the concentrations of Cr and Ni, the root soil samples (~0.2 g) were fully digested with mixed acids (HNO₃: HCl: HF=3:1:1) in a microwave digestion instrument (Multiwave 3000, Anton Paar GmbH). Two heavy metals in all the samples, Cr and Ni, being focused on in this study, were analyzed by a X Series 2 Inductively Coupled Plasma-Mass Spectrometer (Thermo fisher

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Scientific, USA). The uncertainties for Cr and Ni determined, were within 5%.

Fig. 1. The schematic diagram of sampling distribution.

2.2 Data analysis

The geoaccumulation index was identified by Muller [4] and adopted in this study. Hence, the I_{geo} equation was used as:

$$I_{geo} = \log_2 \frac{C_i}{1.5C_0} \quad (1)$$

where C_i is the measured concentration (mg/kg) of Cr and Ni in soil, and C_0 is the background concentration of Cr and Ni in the soils of Anhui Province [5]. The 1.5 constant was used to correct for regional background difference. The contamination could be divided into 6 levels: uncontaminated ($I_{geo} \leq 0$), slightly contaminated ($0 < I_{geo} < 1$), moderately contaminated ($1 < I_{geo} < 2$), moderately to heavily contaminated ($2 < I_{geo} < 3$), heavily contaminated ($3 < I_{geo} < 4$), heavily to extremely contaminated ($4 < I_{geo} < 5$), and extremely contaminated ($5 \leq I_{geo}$) [6].

The potential ecological risk assessment was employed by calculating the potential ecological risk index (RI) of Cr and Ni in the soils surrounding the alunite mining area [7,8]. The following formula was applied for the calculation of RI :

$$C_r^i = \frac{C_i}{C_0} \quad (2)$$

$$E_r^i = T_r \times C_r^i \quad (3)$$

$$RI = E_{Cr}^i + E_{Ni}^i \quad (4)$$

where C_r^i is the enrichment coefficient of heavy metal (Cr and Ni in this study) in soil, E_r^i is the potential ecological risk factor of single element, and T_r is the toxic-response coefficient whose values are 2 and 5 for Cr and Ni, respectively [7]. The potential ecological risk of heavy metals in soils could be classified into five categories based on the values of E_r^i and RI , as detailed in Table 1.

The ability of dominant plants to accumulate heavy metals was expressed by transportation and enrichment coefficients, while transportation coefficient was obtained by the ratio of the heavy metal content in the aboveground part and the value in the underground part, and enrichment coefficient equals the ratio of the heavy metal content between in the aboveground part and in the root soil.

Table 1. Grading standards of potential ecological risk of heavy metal pollution.

Risk factor for single metal	Risk index for multiple metals	Ecological risk level
<40	150	Low
40-80	150-300	Moderate
80-160	300-600	Considerable
160-320	600-1200	High
>320	>1200	Very high

3 Results and discussion

Table 2 summarizes the distribution characteristics of Cr and Ni in sampling root soils. The ranges of soil Cr and Ni contents are 46.20-503.50 and 12.80-44.00 mg/kg, respectively. Compared with their background values, it is identified that mining activities significantly raise the releasing content of heavy metal from alunite mining area into soils surrounding. However, due to the specific element composition of alunite ore, the Cr and Ni pollution is not as serious as expected. According to GB 15618-2018 (National Soil Environmental Quality Criterion, China), Cr and Ni contents in few sampling soils exceed the corresponding risk screening value.

Table 2. The distribution characteristics of Cr and Ni in sampling root soils (mg/kg).

HMs	Max	Min	Background Value ^a	Screening Value ^b
Cr	503.50	46.20	66.50	250.00
Ni	44.00	12.80	29.80	60.00

^a Corresponding heavy metal background values of Anhui Province [5]

^b Risk screening values (pH≤5.5) according to National Soil Environmental Quality Standards, China (GB 15618-2018)

Table 3 summarizes the geoaccumulation index and potential risk index of heavy metals in the root soils surrounding the mining district. The root soils were slightly to extremely polluted with respect to Cr based on the I_{geo} values, while there is significant differentiation of Cr pollution in the studied root soils. Meanwhile, the root soils were only slightly contaminated with respect to Ni, corresponding to the lower concentrations than screening value.

Although the geoaccumulation index of Cr reveals a certain pollution phenomenon, Cr posed the acceptable level of potential ecological risk with E_{Cr}^i values significantly lower than 40. Similarly, Ni had single risk indices below 40, which are indicative of low risk. The RI values suggest that Cr and Ni in the root soils surrounding the typical alunite mining area had negligible potential ecological risk. This positive situation is probably caused by long-term non-exploitation and that chromium and nickel are unimportant constituents to the alunite ore.

Table 3. Geoaccumulation index and Potential risk index of soil Cr and Ni.

Plant Category	I_{geo}		E_r^i		RI
	Cr	Ni	Cr	Ni	
control site (agricultural land)	0.70	0.65	2.11	4.87	6.98
<i>Ophiopogon bodinieri</i> Levl	0.75	0.29	2.24	2.15	4.39
<i>Lysimachia fortune</i> Maxim	0.51	0.42	1.53	3.15	4.68
<i>Bidens pilosa</i> L	5.05	0.98	15.14	7.38	22.52
<i>Haloragis micrantha</i> (Thunb.) R. Br	0.46	0.34	1.39	2.58	3.97
<i>Conyza canadensis</i> (L.) Cronq	0.61	0.60	1.82	4.53	6.35
<i>Pteridium aquilinum</i> (L.) Kuhn var	0.69	0.61	2.07	4.60	6.67
<i>Schisandra chinensis</i> (Turcz.) Baill	1.34	0.67	4.02	5.03	9.05
<i>Phytolacca acinosa</i> Roxb	1.73	0.86	5.20	6.46	11.66
<i>Commelina communis</i> L	2.45	0.98	7.36	7.37	14.73
<i>Viola philippica</i>	1.39	0.65	4.17	4.87	9.04

Table 4. Enrichment and transportation coefficient of dominant plants.

Plant Category	Cr	
	Enrichment Coefficient	Transportation Coefficient
<i>Ophiopogon bodinieri</i> Levl	0.16	2.86
<i>Lysimachia fortune</i> Maxim	0.07	0.86
<i>Bidens pilosa</i> L	nd	0.44
<i>Haloragis micrantha</i> (Thunb.) R. Br	0.15	1.52
<i>Conyza canadensis</i> (L.) Cronq	nd	0.80
<i>Pteridium aquilinum</i> (L.) Kuhn var	0.04	0.88
<i>Schisandra chinensis</i> (Turcz.) Baill	0.02	1.00
<i>Phytolacca acinosa</i> Roxb	0.01	0.56
<i>Commelina communis</i> L	0.01	1.46
<i>Viola philippica</i>	0.03	0.62

nd represents not detectable

As one of the most important remediation methods, phytoremediation is mainly according to the absorption mechanism of dominant plants to heavy metals in the root soil. Hence, the enrichment coefficient and transportation

coefficient were used to characterize the absorption and transportation capacity of dominant plants to Cr in the alunite mining area, which has obviously potential ecological health risk. Table 4 summarizes the calculation results of enrichment and transportation coefficient of dominant plants, based on the determination of Cr contents in the overground and underground parts of dominant plants. The enrichment coefficients of dominant plants to Cr were significantly low, suggested that the ability of dominant plants to accumulate Cr in the studied area was not apparent. However, some typical plants such as *Ophiopogon bodinieri* Levl, *Haloragis micrantha* (Thunb.) R. Br, *Schisandra chinensis* (Turcz.) Baill, and *Commelina communis* L, posed relatively high transportation coefficients, given the opportunity to become part of satisfactory combined remediation.

4 Conclusions

The abandoned alunite mine had relatively high levels of Cr and Ni with respect to background values, while the heavy metal contents are still within the limits of national risk screening values. The accumulation index and potential ecological risk index were calculated, and the result shows that the root soils surrounding the abandoned alunite mining area were not seriously polluted with respect to Cr and Ni. However, different levels of Cr pollution had been identified by the geoaccumulation index, although the single risk index of Cr and the comprehensive potential ecological risk index RI are indicative of low risk. Without the regional influence, it can be concluded that alunite mining activities contribute few Cr and Ni to soils surrounding, caused that this typical alunite mining area had been abandoned for a long time and the mineral composition of alunite ore contain low levels of Cr and Ni. Plants such as *Ophiopogon bodinieri* Levl, *Haloragis micrantha* (Thunb.) R. Br, *Schisandra chinensis* (Turcz.) Baill, and *Commelina communis* L, could be better choices in the consequent remediation of heavy metal pollution.

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