Risk Assessment of Heavy Metal Pollution in Soils of Gejiu Tin Ore and Other Metal Deposits of Yunnan Province

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Abstract. This paper aims to study three main metal mining areas in Yunnan Province, to summarize and analyze the heavy metal pollution situation in each mining area, and to assess the ecological risk of the mining areas. The results showed that heavy metal pollution existed in different regions of the three mining areas with pollution elements of Cd, As, Cu, Pb, Zn. Risk level, besides Zhen Yuan mining area (class C), for the other two areas was class D, with Beichang mining area in Lanping as the most serious polluted mining area.

1. Introduction
Yunnan Province is a province with large mining resources in China. Since the reform and opening-up policy, the mining economy has got a rapid development, which greatly promoted the economic construction and social development of Yunnan Province, especially the polymetallic mining which has played a decisive role in the economic society of Yunnan Province. With the increase of mining scale, the mining area environment suffered serious damage that caused the decrease of natural vegetation, soil, water and air pollution, an increase in soil erosion, decline of slope stability, etc. Thus, already serious landslide and debris flow were further aggravated. The province's mining pollution emissions accounted for half of the province's industrial pollution emissions, and heavy metals in soil had received widely attention. It is because that heavy metals cannot be absorbed or transformed by soil microorganism, while they can enter the food chain by plants absorption, expanding the influence scope, and became a threat to human health [1-2]. Therefore, in this paper, we investigated soil heavy metal pollution in three main metal mining areas of Yunnan Province, namely Gejiu tin ore, Lan Ping lead-zinc ore and Zhen Yuan gold mine (figure 1), assessed the ecological risk of heavy metal pollution, compared and analyzed pollution intensity and characteristics of heavy metal pollution in different mining area, and provided theoretical basis for further heavy metal pollution control in mining areas.
Figure 1. Distribution of studied mining areas in Yunnan

Analysis and assessment were carried out on the basis of the National Soil Environmental Quality Standard (GB15618-1995) [3], as shown in Figure 1. Lars Hakanson [4] ecological risk assessment approach was used for risk assessment, and the calculating formula is as following:

\[
RI = \sum_{i=1}^{n} E_{i}^{r} = \sum_{i=1}^{n} T_{i}^{r} C_{i}^{s} = \sum_{i=1}^{n} T_{i}^{r} C_{i}^{s} / C_{n}^{i}
\]  

(1)

whereas: \( RI \) - Potential ecological risk index of poly-metallic; \( E_{i}^{r} \) - potential ecological harm coefficient of a single heavy metal; \( T_{i}^{r} \) - toxic response coefficient of each heavy metal, Hakanson levels of heavy metals toxicity order: Cd (30) > As (10) > Cu (5) > Pb (5) > Cr (2) > Zn (1); \( C_{i}^{s} \) - pollution coefficient of a single heavy metal; \( C_{s}^{i} \) - measured values of heavy metals in surface sediment; \( C_{n}^{i} \) - reference value required for calculation, usually heavy metals concentration in sediment before mining activities or heavy metals concentration in unpolluted sediment of the control used as reference value.

In this paper, the natural background values of the National Soil Environmental Quality Standard were adopted for calculation. The natural background values were shown in table 1.

2. Heavy metal pollution condition of soil of Gejiu tin ore

Due to the long history of mining and the largest tin deposits, Gejiu was known as the "Tin Capital". Soil heavy metal pollution in this city caused by long-term exploitation has also been paid widespread attention, and the heavy metals survey was conducted gradually.
Table 1. Soil environmental quality standard values

| Elements     | First level | Second level | Third level |
|--------------|-------------|--------------|-------------|
|              | Natural background | <6.5 | 6.5~7.5 | >7.5 | >6.5 |
| Cr (Dry farm) | 90 | 250 | 300 | 350 | 400 |
| Cu (Farmland)| 35 | 50 | 100 | 100 | 400 |
| Pb            | 35 | 250 | 300 | 350 | 500 |
| Zn            | 100 | 200 | 250 | 300 | 500 |
| Cd            | 0.2 | 0.3 | 0.3 | 0.6 | 1.0 |
| As (Dry farm) | 15 | 40 | 30 | 25 | 40 |
| As (Paddy field) | 15 | 30 | 25 | 20 | 30 |

Table 2. Grades of potential ecological risk assessment [4]

| Potential ecological risk factor of single metal (E') | Potential ecological risk | Risk grade | Potential ecological risk index of poly-metallic (RI) | Potential ecological risk | Risk grade |
|--------------------------------------------------------|--------------------------|------------|-------------------------------------------------|--------------------------|------------|
| <40                                                    | Slight                   | A          | <150                                           | Slight                   | A          |
| 40~80                                                  | Moderate                 | B          | 150~300                                         | Moderate                 | B          |
| 80~160                                                 | Strong                   | C          | 300~600                                         | Strong                   | C          |
| 160~320                                                | Very strong              | D          | ≥600                                            | Very strong              | D          |
| ≥320                                                   | Extremely strong         | E          |                                                 |                          |            |

Xiao Qingqing et al. (2011) [5] carried on the sample investigation on crop root zone soil in the farmland of Jijie town, Gejiu from January to February, 2009. The values of Zn, Pb, Cu, Cd were (628.87±17) mg·kg⁻¹ (1185.48±490.72) mg·kg⁻¹ (453.50±129.11) mg·kg⁻¹ and (7.50±5.40) mg·kg⁻¹, respectively, and exceeded the secondary standard of national soil quality 1.09, 2.39, 3.54 and 11.50 times, respectively, which indicated severely contaminated soil and element pollution order: Cd > Cu > Pb > Zn. Li Yanyan et al. [6] investigated the farmland soil near the metallurgy factory of Jijie town, Gejiu in April 2013. According to the secondary standard of national soil quality, they found that the content
of five heavy metals of As, Pb, Cd, Cu and Zn were out of limits, with an exceed of 14.62, 1.55, 14.17, 2.11, 1.04 times of the standard content, and order of heavy metal pollution in farmland: As > Cd > Cu > Pb > Zn. Zhang Yanhong et al. (2010) [7] studied the heavy metal content in sugarcane roots soil surrounding the Gejiu tin industrial and mining areas. Pb, Cr, Cd, Cu content in sampling area soil was 82.06-2052.32 mg·kg\(^{-1}\), 13.77-58.71 mg·kg\(^{-1}\), 11.29-1075.89 mg·kg\(^{-1}\) and 689.09-1923.40 mg·kg\(^{-1}\), respectively, according to , in addition to the Cr, Pb, Cd and Cu were all exceeded the limits of the secondary standard of national soil quality, with values of 6.84, 3583.33, 6.84 times of the standard ones, respectively.

From the above three surveys we can found that the main pollution elements are Pb, Cd, Cu and Zn, As, with As, Cd and Cu heavily polluted the soil. The farmland near Jijie town of Gejiu City in 2009 was took as the No. 1 study area, the farmland near metallurgical plant of Jijie town in 2013 as No. 2 study area, sugarcane field surrounding Gejiu tin industrial and mining area as No. 3 study area for the ecological risk assessment of each element in each area. The results were shown in Table 3 and indicated that three research areas had been seriously polluted with the ecological risk grade of D, in which No. 3 had the highest risk grade, and Cd was the most serious pollution element.

### Table 3. The ecological risk index of the research areas in Gejiu mining area.

| Research area | Pb    | Zn    | Cu    | Cd    | As    | RI    | Level of risk |
|---------------|-------|-------|-------|-------|-------|-------|---------------|
| No. 1         | 47.89 | 8.04  | 16.65 | 64.5  |       | 2265.73 | D             |
| No. 2         | 34.94 | 7.63  | 9.69  | 56.2  | 32.28 | 2239.63 | D             |
| No. 3         | 56.64 | 19.23 | 20.08 | 5375  |       | 161707.84 | D             |

3. Heavy metal pollution condition of soil of Lanping lead and zinc ore

Jinding lead-zinc deposit in Lanping is the largest confirmed lead-zinc mine of China. The annual mining and production of mining area has caused serious heavy metal pollution on the surrounding environment, severely hampered the sustainable development of agriculture and health of organism [8-9]. Li Rui-ping et al (2009) [10] collected and analyzed the bare surface soil of Jinding mining area in Lanping in 2007. The results showed that the average of the total Zn and Cd two elements were 219922.62 mg·kg\(^{-1}\) and 17078.8 mg·kg\(^{-1}\), respectively, with the highest value of 219922.62 mg·kg\(^{-1}\) and 219922.62 mg·kg\(^{-1}\) , respectively, which was 439.85 times and 17078.8 times of the standard ones according to the third standard of national soil. In 2009 [11], the sampling analysis was carried out and the results showed that the average of Pb total content in samples was 9993.31 mg·kg\(^{-1}\), with the maximum value of 31245.54 mg·kg\(^{-1}\), and exceeded the standard value 624.9 times. Tang Yetao et al (2006) [12], carried on sample analysis in Jia Ya Shan and Bei Chang of Lan Ping mining areas, the results showed that three elements Zn, Pb and Cd in the above two areas reached the highest value of
120125 mg·kg⁻¹ and 28878 mg·kg⁻¹, 17625 mg·kg⁻¹ and 13998 mg·kg⁻¹, 2086 mg·kg⁻¹ and 210 mg·kg⁻¹. According to the third grade standard of the national soil quality, Zn, Pb and Cd in Jiayashan area exceeded 240.25, 35.25, 208 times of the standard value, respectively; In Bei Chang Zn, Pb and Cd exceeded 57.76, 28.00, 210 times, respectively.

Table 4. The ecological risk index of the research areas in Lanping mining area.

| Research area | Pb     | Zn     | Cd     | RI          | Level of risk |
|---------------|--------|--------|--------|-------------|---------------|
| No. 4         | 8927.19| 2199.23| 85390  | 2608525.18  | D             |
| No. 5         | 503.57 | 1201.25| 10430  | 316618.85   | D             |
| No. 6         | 399.94 | 288.78 | 1050   | 4853523.68  | D             |

From the previous researches, it can be found that the contamination by heavy metals of Zn, Pb and Cd were serious. Jinding mining area in Lanping was took as the No. 4 study area, Jiayashan as No.5 study area, Beichang as No. 6 study area, for the ecological risk assessment of each element in each area. The results were shown in Table 4 and indicated that three research areas had been seriously polluted with the ecological risk grade of D, in which Cd is the most serious pollution element.

4. Heavy metal pollution condition of soil of Zhen yuan mining area
Since the discovery of Zhen Yuan gold ore in 1980s, the total exploitation time is long, this caused a serious damage on the ecology of the mining area.

Yang Shuran et al. (2012) [13] conducted a river sediment sampling analysis in the mining area in 2012, the results showed that the highest value of As was 454 mg·kg⁻¹, which exceeded 15 times of the third grade standard of the national soil quality, with pollution risk index of single metal of 30.27, the comprehensive ecological risk index of 300.27, the risk level of class C.

5. Conclusion
After the analytic investigation on the heavy metal element content in the above three main mining areas, the following conclusions can be reached: Pb, Zn, Cu, Cd and As were the pollution elements in the nearby soil of Gejiu tin ore mining area, including Cd as the most polluted element. Zn, Pb and Cd were the pollution elements in the soil of Lanping lead-zinc mining area with Cd as the most polluted element. As is the most serious pollution element in Zhen Yuan gold mining area; Through the ecological risk assessment, in addition to Zhen Yuan gold river sediment rating was class C, the ecological risk index of the other two mining areas were class D; After comparison of pollution degree among the three mining areas, it can be found that the highest comprehensive ecological risk index was Lanping lead-zinc mining area, with Beichang being contaminated most seriously.
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