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Heavy Metal Risk Assessment of Soils and Crops in the Intensive Mining Area of Gejiu, Yunnan Province

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Abstract

In order to investigate the heavy metal contamination of soil-crop in mining-intensive areas of Gejiu stannary in Yunnan Province and its risk to human health, the single-factor contamination index method and the Nemero comprehensive contamination index method were used to evaluate the contamination risk of heavy metals (Cd and As) in the soil of mining-intensive areas, and the health risk evaluation model was used to study the risk brought by residents through the consumption of maize, wheat and broad beans. The results showed that the mean values of total As and Cd in the soil of the study area were 146 and 2.32 mg·kg^{-1}, which were 8 and 10.5 times higher than the background values of soil environment in Yunnan Province and belonged to heavy pollution; the enrichment coefficients of As and Cd in maize were 0.1% and 5.7%, in wheat were 0.3% and 11.5%, in fava beans were 0.1% and 4.9%; the soil contamination indices in the four study areas of A, B, C, and D were 7.275, 6.797, 5.618, and 5.060, respectively. The results indicated that the soils in the study areas belonged to heavy contamination levels, and the enrichment ability of Cd in all three crops was stronger than that of As, with wheat being the strongest, As in the three crops and Cd in broad beans might be harmful to children. As in wheat and broad beans may be harmful to adults.

Keywords

Heavy Metal Pollution, Cadmium, Arsenic, Risk Assessment, Mining Areas

1. Introduction

As a receptor for pollutants from natural, industrial, agricultural, and anthropogenic activities, most pollutants are retained in the soil through natural activities, causing some degree of harm to the soil ecosystem (Wei et al., 2020). With the rapid economic development in China and the increase of industrialization, urbanization, and rural intensification, a serious problem has emerged-soil heavy metal pollution. Soil heavy metal contamination of agricultural land is related to soil ecosystem stability, food safety, and human health risks (Song et al., 2018). Most studies have shown (Li et al., 2019) that mineral dust generated during mining activities is dispersed into the soil around the mine site through atmospheric deposition. Also, irrigation and fertilization in agricultural production activities is one of the most important causes of soil heavy metal pollution (Feng et al., 2020). Soil heavy metal pollution in China mainly includes Cd, Hg, Pb, Cr, Cu, Zn, Ni, etc., and metalloid As (Yu et al., 2021).

According to relevant statistics, the area of arable land contaminated by heavy metals such as Cd and As currently occupies roughly 1/5 of the arable land area nationwide, nearly 25 million·hm^2 (Gao, 2013). Cd is classified as a human carcinogen by the National Toxicology Program and the International Agency for Research on Cancer (Friberg & Vahter, 1983) because of the high residual characteristics of heavy metals that do not disappear even if they continue to accumulate in the food chain, and its high toxicity can cause great harm to the human body (Cai et al., 2018). It has been shown (Wang et al., 2010; Zhang et al., 2020) that soil Cd has caused serious contamination of vegetables and rice, and that vegetables are more enriched in Cd than rice. Zhao Ruixin (2004) concluded that the As content in virgin soils is generally not very high and is influenced by anthropogenic activities and contains high As concentrations in soils in areas around mines and factories. Chen Guoliang et al. (2017) found that As is not an essential element for plant growth. However, at smaller concentrations of As, it can accelerate crop growth, kill harmful microorganisms in plants, accelerate plant control of As, and indirectly affect the uptake of other elements, while high levels of As can hinder crop growth.

The city of Gejiu, Yunnan Province, also known as the "tin capital", is an industrial city with a non-ferrous metal industry (Ran et al., 2019), and with the development of the city, urban industrial pollution is becoming more and more serious. The study found (Zhang et al., 2022) that the investigation of heavy metal contamination of agricultural soils and crops in the tin mining area of Gejiu found that Pb, As, Cd, Cu, and Zn were seriously contaminated in the soil, wheat, radish and peas in the mining activity area were contaminated with heavy metals. Xiao Qingqing et al. (2011) investigated heavy metal contamination of crops in Jijie Town, Gejiu City, and found that mint, lettuce and bok choy had high uptake of Pb, Zn, Cu and Cd and were not suitable for continued cultivation in contaminated areas. Some studies have shown (Ran et al., 2019) that the soil in the intensive mining area of Gejiu is mainly a compound contaminated soil with Cd and As, and few articles have studied Cd and As in the intensive mining area and their effects on wheat, maize, and broad beans; therefore, in this paper, the risk evaluation of Cd and As contamination of soil and agricultural crops in the intensive mining area of Gejiu is intended to analyze the degree of contamination of agricultural land in the intensive mining area of Gejiu and the evaluation of ecological risks through the Nemero comprehensive pollution index method and the human health risk evaluation method to provide a reference basis for restoring the ecological environment and preventing soil pollution.

2. Materials and Methods

2.1. Study Area

Located in the southeastern part of Yunnan Province, the dense mining area of Gejiu City covers an area of 1587 km^2, with an urban elevation of 1688 m, a minimum height of 150 m and a maximum height of 2740 m. With a longitude of 102˚54' to 103˚25' east and a latitude of 23˚01' to 23˚36' north, it has a subtropical plateau monsoon climate with hot summers and very cold winters, abundant precipitation, four seasons like spring, an average annual temperature of 16˚, a high temperature of 29˚ in summer and rare temperatures below the freezing point. The effective irrigated area of perennial arable land in Gejiu City is 10,800 ha, and the irrigated area of reduced arable land is 760 ha, so the first major economic industry is agriculture. According to the detailed survey of the soil pollution status of agricultural land in Yunnan Province, the farmland soil and crops in Gejiu are more seriously affected by heavy metals.

2.2. Sample Collection

In accordance with the single point sample sampling, a certain dense mining area and surrounding areas in Gejiu City were selected, from left to right, from top to bottom, four sampling areas were A, B, C and D areas around the mining area of the aluminum plant, as show in **Figure 1**. A total of 14 soil and crop samples were collected from four areas, four from area A, three from area B, three from area C and four from area D. The plants were washed, dried, ground fine and sieved, and then the soil was mixed, dried, ground fine and sieved.

2.3. Test Items and Methods

Soil arsenic according to GB/T 22105.2-2008 "Soil quality Determination of total mercury, total arsenic, total lead Atomic fluorescence method" Part 2: Determination of total arsenic in soil detection, soil cadmium according to DZ/T 0279.5-2016 "Regional geochemical sample analysis method" Part 5: Determination of cadmium amount Inductively coupled plasma mass spectrometry detection, arsenic and cadmium in crops according to GB 5009.268-2016 "Food safety national standard for the determination of multiple elements in food in food" detection.

2.4. Evaluation Methods and Evaluation Criteria

1) Soil evaluation methods

Single pollution index method:

$$P_i = C_i / S_i \tag{1}$$

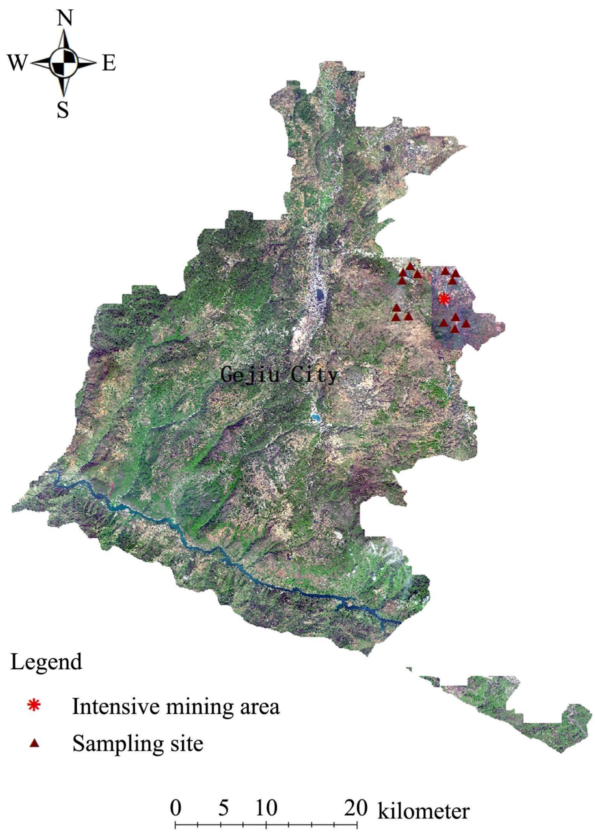

Figure 1. Samples collection points in the study area.

P_i is the single factor pollution index of pollutant i in crops. C_i is the measured data of pollutant i in crops; S_i is the evaluation standard of pollutant i.

Nemero integrated pollution index method takes into account the average and maximum value of the single-factor pollution index, which can reflect the role of the more serious pollution of heavy metal pollutants, and the integrated pollution index method is calculated as follows:

$$P_n = \sqrt{\frac{\overline{P}^2 + P_{i\max}^2}{2}} \quad (2)$$

where P_n is the integrated pollution index of the sampling point; $P_{\max}$ is the maximum value in the single-factor pollution index of soil heavy metal pollution at the i sampling point; $\overline{P} = \frac{1}{n}\sum_{i=1}^{n} P_i$ is the average value obtained from the single-factor index.

2) Crop evaluation methods

To study the health risk of the population through the consumption of corn, wheat and fava beans, a health risk evaluation model was used to evaluate the local contamination with the following equation:

$$\text{HQ} = \frac{\text{ADD}}{\text{RFD}} \quad (3)$$

where HQ is the health risk index, RFD is the reference dose of heavy metal exposure, [mg·(kg·d)$^{-1}$], and ADD is the average daily intake of contaminants via food crops, [mg·(kg·d)$^{-1}$]; when HQ ≤ 1, it means that heavy metals in crops do not cause human health risk. When HQ > 1, it means that heavy metals can cause human health risk, and the larger the health risk index indicates the higher the human health risk.

The ADD in the above equation is calculated as follows:

$$\text{ADD} = \frac{C_i \times I \times EF \times ED}{BW \times AT} \tag{4}$$

where C_i is the amount of heavy metal i in the crop, (mg·kg^{-1}); I human daily intake of the crop (kg·d^{-1}); EF exposure frequency (d·a^{-1}); ED exposure time (a); BW recipient body weight (kg); AT life expectancy (d).

3. Results and Analysis

3.1. Soil Arsenic and Cadmium Pollution

3.1.1. Soil Total Arsenic and Cadmium Content

The coefficient of variation can indicate the discrete level of heavy metal elements in space. For small fluctuations, a rate of change less than 15 can be called low variation; a rate of change greater than 36 is a case of higher variation and can be called high variation; a rate of change from 15 to 36 is an average change and can be called medium variation. As shown in Table 1, the coefficient of variation of the full As around the dense mining area A in Gejiu is 38.4%, which is high variation; the coefficient of variation of the full As in area B is 2.0%, which is low variation; the coefficient of variation of the full As in area C is 10.9%, which is low variation; the coefficient of variation of the full As in area D is 9.7%, which is low variation, and the full As in the overall area is medium variation; the coefficient of variation of the full Cd in area A The coefficient of variation of the full Cd in region A was 29.5%, which was moderate; the coefficient of variation of the full Cd in region B was 8.7%, which was low; the coefficient of variation of the full Cd in region C was 9.3%, which was low; the coefficient of variation of the full Cd in region D was 5.6%, which was low; and the full Cd in the overall region was moderate. This shows that the dispersion of As and Cd elements content is medium and the content distribution is relatively uneven.

Using the soil risk screening value as a criterion to calculate how many samples exceeded the standard, it is known from Table 1 that the range values of total As and Cd in the soil of area A are 109 - 245 mg·kg^{-1} and 1.64 - 3.35 mg·kg^{-1} respectively; The range values of total As and Cd in soils in area B were 144 - 150 mg·kg^{-1} and 2.49 - 2.94 mg·kg^{-1}, respectively; the range values of total As and Cd in soils in area C were 129 - 160 mg·kg^{-1} and 2.02 - 2.40 mg·kg^{-1}, respectively; The range values of total As and Cd in the soil of area D were 117 - 148 mg·kg^{-1} and 1.85 - 2.12 mg·kg^{-1}, respectively. The exceedance rate of As and Cd in the soil of the study area is 100%, which far exceeds the background value of soil quality in Yunnan Province, and should be promptly controlled to strengthen the protection and treatment of the soil in the area.

Table 1. The total amount of heavy metal in the soil of the study area.

Region	Heavy Metals	Range Value ($mg \cdot kg^{-1}$)	Median ($mg \cdot kg^{-1}$)	Average ($mg \cdot kg^{-1}$)	Standard deviation ($mg \cdot kg^{-1}$)	Coefficient of variation (%)
A	As	109 - 245	146.5	161.75	53.81	38.4
	Cd	1.64 - 3.35	2.49	2.49	0.636	29.5
B	As	144 - 150	147	147	2.45	2
	Cd	2.49 - 2.94	2.61	2.68	0.19	8.7
C	As	129 - 160	141	143.33	12.76	10.9
	Cd	2.02 - 2.40	2.09	2.17	0.165	9.3
D	As	117 - 148	132.5	132.5	11.1	9.7
	Cd	1.85 - 2.12	2.01	2	0.097	5.6
Total	As	109 - 245	142.5	146.29	31.99	22.7
	Cd	1.64 - 3.35	2.17	2.32	0.451	20.1

Note: The pH of the tested farmland soil samples were all in the range of 6.5 to 7.5, and the limit value of As soil quality standard was 30 $mg \cdot kg^{-1}$; the limit value of Cd soil quality standard was 0.6 $mg \cdot kg^{-1}$.

3.1.2. Evaluation of Soil Single Factor Index and Integrated Pollution Index

As shown in Table 2 and Table 3, with the background evaluation standard of soil quality in Yunnan Province, the calculation of soil single factor index and comprehensive pollution index can be carried out. As shown in Table 4, soils in area A have an As one-factor index of 0.879, which is less than 1, and are clean soils; soils in area B have an As one-factor index of 0.799, which is less than 1, and are clean soils. The As one-factor index of soil in area C is 0.779, which is less than 1 and belongs to clean soil; the As one-factor index of soil in area D is 0.720, which is less than 1 and belongs to clean soil. The Cd single factor index of soil in area A is 11.332, which is greater than 3 and belongs to heavily polluted soil; the Cd single factor index of soil in area B is 12.182, which is greater than 3 and belongs to heavily polluted soil; the Cd single factor index of soil in area C is 9.864, which is greater than 3 and belongs to heavily polluted soil; the Cd single factor index of soil in area D is 9.068, which is greater than 3 and belongs to heavily polluted soil. The comprehensive pollution index of soil in area A is 7.275, which is more than 3 and belongs to heavily polluted soil; the comprehensive pollution index of soil in area B is 6.797, which is more than 3 and belongs to heavily polluted soil; the comprehensive pollution index of soil in area C is 5.618, which is more than 3 and belongs to heavily polluted soil; the comprehensive pollution index of soil in area D is 5.060, which is more than 3 and belongs to heavily polluted soil; As in the overall area was determined for lightly contaminated soil and Cd was determined for heavily contaminated soil.

Table 2. P_i and P_n grading criteria.

	Single factor pollution index	Pollution degree	Integrated Pollution Index	Pollution degree
1	$P_i < 1$	Cleaning	$P_n \leq 0.7$	Safety
2	$1 \leq P_i < 2$	Light contamination	$0.7 < P_n \leq 1$	Alert level
3	$2 \leq P_i < 3$	Medium contamination	$1 < P_n \leq 2$	Light contamination
4	$P_i \geq 3$	Heavy contamination	$2 < P_n \leq 3$	Medium contamination
5			$P_n > 3$	Heavy contamination

Table 3. Soil environmental quality soil pollution risk control standards for agricultural land (GB15618-2018).

Item	pH	Cd ($mg \cdot kg^{-1}$)	As ($mg \cdot kg^{-1}$)
Soil risk screening values	6.5 - 7.5	0.3	30
Soil risk control values	6.5 - 7.5	3.0	120
Background of soil quality in Yunnan Province		0.22	18.40

Table 4. P_i and P_n values of heavy metals in crops.

Region	P_i (As)	P_i (Cd)	P_n
A	0.879	11.332	7.275
B	0.799	12.182	6.797
C	0.779	9.864	5.618
D	0.720	9.068	5.060

3.2. Arsenic and Cadmium Contamination of Crops in the Study Area

3.2.1. Analysis of Arsenic and Cadmium Levels in Crops in the Study Area

The enrichment capacity of heavy metals may vary greatly depending on the crop. As shown in **Table 5**, it is known in conjunction with **Table 6**, the values of As in maize ranged from 0.051 to 0.374 $mg \cdot kg^{-1}$ with an enrichment factor of 0.1%; As in wheat ranged from 0.315 to 0.584 $mg \cdot kg^{-1}$ with an enrichment factor of 0.3%; As in broad beans ranged from 0.161 to 0.307 $mg \cdot kg^{-1}$. The enrichment coefficient was 0.1%. The analysis continued and it was found that the As content in the two samples of corn and beans did not exceed the limit of arsenic in food, while the As content in the wheat samples partially exceeded the limit of arsenic in food, and As was also the highest enrichment factor in the wheat crop, followed by corn and beans. The values of Cd in maize ranged from 0.011 to 0.271 $mg \cdot kg^{-1}$ with an enrichment factor of 5.7%; Cd in wheat ranged from 0.211 to 0.241 $mg \cdot kg^{-1}$ with an enrichment factor of 11.5%; and Cd in broad beans

Table 5. Content of heavy metals in crops.

Crop type	Heavy Metals	Range Value (mg·kg^{-1})	Median (mg·kg^{-1})	Average (mg·kg^{-1})	Standard deviation (mg·kg^{-1})	Coefficient of variation (%)	Enrichment factor (%)	Limit value (mg·kg^{-1})
Corn	As	0.051 - 0.374	0.093	0.144	0.107	79.1	0.1	0.5
	Cd	0.011 - 0.271	0.097	0.125	0.111	94.6	5.7	0.1
Wheat	As	0.315 - 0.584	0.45	0.45	0.135	42.3	0.3	0.5
	Cd	0.221 - 0.241	0.231	0.231	0.01	6.1	11.5	0.1
Fava beans	As	0.161 - 0.307	0.257	0.246	0.054	25.4	0.1	0.5
	Cd	0.084 - 0.188	0.129	0.132	0.037	32.7	4.9	0.1

Note: Heavy metal enrichment factor = heavy metal content in the crop/content of that heavy metal in the soil × 100%.

Table 6. Values of crop health risk evaluation parameters.

Evaluation Parameters	Crop type	Adult reference values	Reference values for children
I/kg·d^{-1}	Corn	0.15 (Zhou et al., 2020)	0.10
	Wheat	0.20 (Tao et al., 2017)	0.15
	Fava beans	0.45 (Yu et al., 2019)	0.23
EF/d·a^{-1}	/	320	350
ED/a	/	25	6
AT/d	/	10950	3650
BW/kg	/	56.8	15.9

Note: The three crops selected for this study were the actual crops grown at the sampling site.

ranged from 0.084 to 0.188 mg·kg^{-1} with an enrichment factor of 4.9%. All three crops had higher enrichment coefficients for Cd than As, so the three crops had stronger enrichment capacity for Cd, from strong to weak for wheat, maize and broad beans respectively.

3.2.2. Human Health Risk Assessment

As shown in Table 7, the adult health risk value for As in corn is 0.926, which is less than 1 and does not pose a risk to adults; the adult health risk value for As in wheat is 3.859, which is greater than 1 and may pose a risk to adults; and the adult health risk value for As in fava beans is 4.746, which is greater than 1 and may pose a risk to adults. The child health risk value for As in corn is 1.737, which is greater than 1 and may be harmful to children; the child health risk value for As in wheat is 8.14, which is greater than 1 and may be harmful to children; and the child health risk value for As in fava beans is 6.825, which is greater than 1 and may be harmful to children. The adult health risk value for Cd in corn is 0.241, less than 1, which is not harmful to adults; the adult health

Table 7. Crop HQ values.

Crop	Adult HQ (As)	Child HQ (As)	Adult HQ (Cd)	Child HQ (Cd)
Corn	0.926	1.737	0.241	0.452
Wheat	3.859	8.142	0.594	0.836
Fava beans	4.746	6.825	0.764	1.097

risk value for Cd in wheat is 0.594, less than 1, which is not harmful to adults; the adult health risk value for Cd in fava beans is 0.764, less than 1, which is not harmful to adults; The child health risk value for Cd in corn is 0.452, which is less than 1 and will not cause harm to children; the child health risk value for Cd in wheat is 0.836, which is less than 1 and will not cause harm to children; the child health risk value for Cd in fava beans is 1.097, which is greater than 1 and may cause harm to children.

4. Discussions

It was found that the soil Cd and As contents in the study area far exceeded the background values of soil quality in Yunnan Province, due to the rich mineral resources in Honghe Prefecture, and Gejiu is the concentration of the main mineral resources in Honghe Prefecture, the non-ferrous metal reserves are the first in the province, and the tin reserves in Jiemao is the first in the country, the soil itself has a high Cd content and the influence of anthropogenic activities such as mining leads to an increase in Cd content. It was found that Pb, Cd, and As exhibit extremely high risks in the tin mining activity area in Gejiu, Yunnan, and are priority elements for mining activity management (Huang et al., 2014). Qiao Pengwei et al. (2013) found that Cd heavy contaminated areas were related to the dominant wind direction, As were more influenced by mining activities, and were related to the distribution of smelters and tailing ponds around the tin mining area in Gejiu. Zeng Min et al. (2019) showed that the soils of Gejiu city are heavily polluted and are a composite of Cd and As, which is consistent with the study that concluded that both As and Cd are heavily polluted in the soils of the intensive mining area of Gejiu. The crop is more enriched in Cd, in the following order: wheat > maize > fava beans, but Cd in maize and wheat is not harmful to adults and children, while Cd in fava beans may be harmful to children, probably because the daily human intake of fava beans is more than that of wheat and maize.

It is noteworthy that both As and Cd are heavily contaminated in the soils of the study area, but the results show that As in maize and Cd in broad beans do not pose a risk to adult human health. Crops grown from heavily polluted soil will not cause harm to humans, probably because the measurement sample is small, the measurement process produces certain errors, the follow-up can strengthen soil environmental monitoring and crop monitoring, expand the measurement range, improve the measurement method, so as to better analyze and discuss the soil and crops in the dense mining area of Gejiu, and provide a more powerful and accurate data base for the subsequent governance.

5. Conclusion

1) The exceedance rates of soil As and Cd in the study area were 100%, and the average values of total As and Cd were 146 and 2.32 mg·kg^{-1}, which were heavily polluted.

2) The enrichment coefficients showed that the crops were more enriched in Cd, in the following order: wheat, maize and broad bean. The enrichment capacity for As was the strongest for wheat, followed by maize and broad bean.

3) Human health risk assessment: As in corn is not hazardous to adults but may be hazardous to children; As in both wheat and fava beans may be hazardous to adults and children. Cd in corn and wheat is not hazardous to adults and children; Cd in fava beans is not hazardous to adults, but may be hazardous to children.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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