Evaluation of Soil Fertility and Heavy Metal Contamination in Abandoned Regions of Tin Mine,China

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KEYWORD: Mine tailings; Soil fertility; Heavy metal contamination; Contamination assessment

ABSTRACT: Based on determination of the contents of soil nutrients elements and heavy metals for the four tin mine tailings (Niubahuang, Laochang, Kafang and Southern) in Gejiu, the heavy metal pollution of four tin mine tailings were assessed with the single contamination index method, the comprehensive contamination index method, the geoaccumulation index method and the potential ecological risk index method. The results showed that:(1)Soil pH of four tin mine tailings was more than 7.5, for alkaline soil. The soil fertility of four tin mine tailings was poor, the soil organic matter soil fertility levels were between VI level, total N、P、K and available P index of soil fertility level basically in III ~ VI, soil fertility index of K available were grade II, the soil fertility order: the Laochang > the Kafang > the Southern > the Niu banghuang. (2)In the four tin mine tailings, the average contents of Mn, Cu, Pb, Cd and Zn were 5700.98mg/kg, 2041.19mg/kg, 7164.72mg/kg, 21.33mg/kg and 2146.81mg/kg. According to the mean size sorting are: Pb＞Mn＞Zn＞Cu＞Cd. According to the single contamination index and the comprehensive contamination index , all of heavy metal contamination grades were high pollution. According to the Hankanson potential ecological risk index evaluation results: Mn and Zn minor ecological risk, Cu, Pb and Ca for strong ecological risk. Cumulative Index to evaluate the results: Mn pollution level was 3, Cu, Pb, Cd contamination level were 6, Zn pollution level was 4 to 5.

INTRODUCTION

Mine tailings is used to refer to the land by destruction or pollution in the process of mining production without governance and hard to use, such as waste rock pile up, abandoned mining land, tailings, etc. China is one of the world's countries with much more mine tailings, the increasing of mine tailings and extremely tense land resources become to a pair of sharp contradictions. It is urgent for the ecological rehabilitation and reclamation. However, the soil structure in the mine tailings is very poor and lack of nutrients with very high content of heavy metal, as well as with very big differences of soil heavy pollution, pollutant type and soil arid condition in different mine tailings, and very difficult for vegetation restoration. Therefore, during the vegetation restoration of the wasted lands, to understand the soil fertility condition and heavy metals pollution condition is very important for the restoration. Gejiu is a super large mining area for tin and copper polymetallic, it is clear that the cumulative non-ferrous metals reserves 4.76 million tons, of which,the tin deposit of 1.7211 million tons, mining result in large area of abandoned land in Gejiu. In view of this, the analysis on the samples taken from the four mine tailings (Niubahuang, Laochang, Kafang and Southern) of Gejiu were made in this paper in order to study the soil heavy metal pollution condition in the individual mine tailing so as to provide a scientific basis for the governance and ecological restoration in a proper way.

MATERIALS AND METHODS

Brief introduction of Project site

Gejiu city, with its famous name of "tin capital" in the world, is located in the south ofYunnan, across between E103 ° 28 '07' ~ 103 ° 09 '14, "N23 18' 56 ° ~ 23 ° 21 '39", it is a industrial city for the production of lead, Zn, copper and other non-ferrous metals with focus on tin production. With high difference in elevation and very clear vertical climate distribution, it covers five climate zones, including north tropics, south Asian tropical, subtropical, tropical north and south temperate zone. Short-time sunlight throughout the year, small difference in annual temperature, long frost-free period and clearly dry and rainy seasons. Mild climate, annual average sunlight 1986.6 h, annual average temperature 16.4 ℃, annual rainfall of 890 mm. Soil types in Gejiu are varied and soil distribution in different elevation, such as latosolic red soil, red soil, yellow soil, yellow brown soil, limestone soil. The four mine tailings (Niubahuang, Laochang, Kafang and Southern) were selected for the study.

Sample collection and pretreatment

Sample collection: The field investigation and sample collection in the four sites was made in June 2014 in Gejiu, according to the terrain characteristics of abandoned land in the four sites, as well as the requirements of "Technical Specification for Soil Environmental Quality Monitoring (NY/T395 2000)", respectively by the methods of "S" points and strip points for sampling, 0 ~ 20 cm of surface soil was collected from the 14 sampling points, each soil sample consists of soil samples collected from multiple points and divided by four points. About 1 kg of each sample was taken and put in bag with label for the laboratory analysis.

Determination method

The determination of soil nutrients: soil pH measurement according to the method of "Analysis of Soil Agro-chemistry", a 1:2.5 ratio method was used to determine soil and water conservation; Determination of soil organic matter—heated potassium dichromate oxidation—external heating method; Soil total nitrogen, hydrolyze nitrogen determination—the solution diffusion method, alkali solution diffusion method; Soil total phosphorus, available phosphorus—alkali soluble - molybdenum antimony colorimetric method and extraction using hydrochloric acid - sulfuric acid; Soil total potassium, available potassium, alkali soluble - flame photometry, 1 mol/L acetic acid ammonium leaching - flame photometry.

The determination of soil heavy metals: soil samples using $HNO_3 + HCl + HClO_4$ (4 ml + 1 ml + 1 ml), flame atomic absorption spectrophotometric method was used for the determination of Mn, Pb, Cu, Cd, Zn content.

Evaluation of heavy metal pollution and its standard

Single contamination index method

Single contamination index method is one of the domestic general evaluation of soil, water, atmosphere and the method of river sediment pollution of heavy metals, the calculation formula: $P_i = \frac{C_i}{S_i}$,

P_i - certain heavy metal elements in soil mass fraction of i; C_i - measured concentration of heavy metal elements in soil, mg/kg. S_i - the threshold of heavy metals i in classIII according to soil environment quality standard (GB 15618-1995), mg/kg.

Comprehensive contamination index method

Nemerow index method is one of the most commonly used method currently at home and abroad to calculate comprehensive pollution index, which is a kind of environmental quality index for both maximum extreme or prominent type weighting contamination, the calculation formula:

$$Pc = \sqrt{\frac{\left[(\overline{P_i})^2 + [\max(P_i)]^2\right]}{2}}$$

in which Pc -soil heavy metal pollution index; $\overline{P_i}$ - the average index of heavy metal elements in soil; $\max(P_i)$ - the greatest single contaminants in the soil pollution index.

Table 1 The classification of soil heavy metal pollution standards

class	Single contamination index(P_i)standard		Comprehensive contamination index(P_C)standard	
	index	class	index	class
I	$P_i \le 0.7$	clean	$P_C \le 0.7$	safe
II	$1 \le P_i < 2$	Mild pollu-	$0.7 < P_C \le 1$	alert
III	$2 \le P_i < 3$	Moderate	$1 < P_C \le 2$	Mild pollu-
IV	$P_i \ge 3$	Heavy pollu-	$2 < P_C \le 3$	Moderate
V			$P_C > 3$	Heavy pollu-

Geoaccumulation index method

Geoaccumulation index method is scientists at the university of Heidelberg, Germany Institute of Sediment Mr. Muller proposed in 1969, and which has been popular used by scholars both at home and abroad for the assessment of soil heavy metal pollution in recent years, its computation formula is:

$$I_{geo} = \log_2\left(\frac{C_n}{k \times B_n}\right)$$

I_{geo} - accumulated index; C_n - the measured values of heavy metal elements in the sample, mg/kg; B_n - geochemical background values of the element

Table2 The relation between geoaccumulation index and pollution degree

I_{geo}	$I_{geo} < 0$	$0 \le I_{geo} < 1$	$1 \le I_{geo} < 2$	$2 \le I_{geo} < 3$	$3 \le I_{geo} < 4$	$4 \le I_{geo} < 5$	$I_{geo} > 5$
Class	0	1	2	3	4	5	6
Pollutiondegree	non	Mild to middle	middle	Middle to heavy	heavy	Heavy to extreme heavy	Extreme heavy

in the sediments. In this study, the soil environmental quality background value of Yunnan province was used as the background value, mg/kg; K - correction coefficient, the value of 1.5.

Potential ecological risk index method

Potential ecological risk index method for the assessment was proposed by a 1980 Swedish scientist Mr. Hakanson in 1980 from the point of view of sedimentology, used in assessment of soil or sediment degree of heavy metal pollution and potential ecological risk, the calculation formula is:

$$(RI)=\sum_{i=1}^{n} E_r^i \quad (1\text{-}4)$$

Of which, the single potential ecological risk index

$$(E_r^i)=T_r^i \times C_f^i \quad (1\text{-}5)$$

The pollution of heavy metal pollutants coefficient

$$(C_f^i)=C_s^i / C_n^i \quad (1\text{-}6)$$

Among them, C_s^i - measured content of heavy metal elements i in soil, mg/kg; C_n^i - to calculate the required ratio value , generally in the evaluation the soil environmental standard values of the country used as a reference ratio, mg/kg.) ; T_r^i is for a single pollutant toxicity response parameters.

Table3 The Hankanson potential ecological risk evaluation and classification relations

Potential ecological risk E_r^i scope	Single contamination risk degree	Potential risk index scope RI <	Total potential risk degree
E_r^i<40	mild	≤RI <150	Mild
40≤E_r^i<80	moderate	150≤RI <300	Moderate
80≤E_r^i<160	heavy	300≤RI <600	heavy
160≤E_r^i<320	Very heavy	RI ≥600	Very heavy
E_r^i≥320	Extreme heavy		

RESULT AND ANALYSIS

Soil Nutrients content in mine tailing

Table4 The Contents of soil nutrient elements in different mine tailings

Site	pH	Organic matter(g/kg)	N		P		K	
			Total N (g/kg)	Hydrolyzable N(mg/kg)	Total P (g/kg)	Effective P (mg/kg)	Total K (g/kg)	Available K (mg/kg)
Niubahuang	7.82	4.691	0.801	116.45	0.423	3.348	10.612	175.328
Laochang	7.78	1.476	1.161	170.188	0.461	9.971	9.553	193.171
Kafang	7.61	7.414	0.726	154.630	0.722	7.751	8.965	160.173
southern	7.68	2.671	0.433	83.545	0.896	10.972	16.833	129.397

Table5 The classification of soil nutrient standards

Nutrient	Organic matter(g/kg)	Total N (g/kg)	Hydrolyzable N(mg/kg)	Total P (g/kg)	Effective P (mg/kg)	Total K (g/kg)	Available K (mg/kg)
I	＞40.00	＞2.00	＞150.00	＞1.00	＞40.00	＞25.00	＞200.00
II	30.00～40.00	1.50～2.00	120.00～150.00	0.80～1.00	20.00～40.00	20.00～25.00	150.00～200.00
III	20.00～30.00	1.00～1.50	90.00～120.00	0.60～0.80	10.00～20.00	15.00～20.00	100.00～150.00
IV	10.00～20.00	0.75～1.00	60.00～90.00	0.40～0.60	5.00～10.00	10.00～15.00	50.00～100.00
V	6.00～10.00	0.50～0.75	30.00～60.00	0.20～0.40	3.00～5.00	5.00～10.00	30.00～50.00
VI	＜6.00	＜0.50	＜30.00	＜0.40	＜3.00	＜5.00	＜30.00

(Note: a:I- very rich, II-rich, III-appropriate amount, IV-less, V-more less,VI-much more less)

The determination results of the soil nutrient elements are shown in table 4. Soil pH measurement results shows that the soil pH were greater than 7.5 (when to neutral soil pH at 6.5 ~ 7.5), as the alkaline soil, showed that the soil acidification did not happen. Table 4 shows that soil fertility levels in different mine tailings are varied. According to soil fertility index classification reference index 5, in general the soil fertility level in the four sites level is lower, the grading index can be seen in table 6 on the basis of nutrient grading standards promulgated by the 2^{nd} national soil census.

The table 6 shows that the level of the organic soil fertility index mostly at level VI, and total N, total P and soil fertility index such as effective P and total K almost at level between III ~ VI basically, available K of soil fertility index mostly at level II. The result shows that the organic matter, total N, total P, effective P and total K become the main factors limiting the soil fertility in tin mine tailings. The order for the soil fertility in the four sites is: Laochang > Kafang >Southern >Niubahuang. The determination results are the same as the research result by Lei Dongmei (2007), Wang Lanyan (2011) and others.

Table6 The soil fertility grade of different mine tailings

Mine tailing site	**Organic matter**	**N**		**P**		**K**	
		Total N	**Hydrolyzable N**	**Total P**	**Effective P**	**Total K**	**Available K**
Niubahuang	VI	IV	III	IV	V	IV	II
Laochang	VI	II	I	IV	IV	V	II
Kafang	V	V	I	III	IV	V	II

Table7 The analysis of the characteristics of heavy metal content of wasteland soil

site	**Mn(mg/kg)**	**Cu(mg/kg)**	**Pb(mg/kg)**	**Cd(mg/kg)**	**Zn(mg/kg)**
Niubahuang	6091.7425±580.7169	2836.1148±994.6643	7256.8967±2261.4010	24.1415±12.8574	2514.6514±601.6313
Laochang	5602.3481±1950.1010	2402.2517±969.8359	6253.8750±1823.6680	34.2361±19.5378	1834.8240±540.0265
Kafang	5410.8190±1109.6250	1572.4359±792.0118	7832.8820±2469.134	15.8387±9.7998	2626.4840±1280.7840
Southern	5699.0490±1875.748	1485.8745±832.1135	7315.5240±2576.2220	11.1016±7.5525	1611.2640±180.3292
Class II	/	50.00	250.00	0.3000	200.00
Class III	/	400.00	500.00	1.000	500.00
Soil environment background value of YN	515.00	28.70	35.70	0.083	86.00

Table8 The heavy metal pollution of wasteland soil index of single contamination and Nemero comprehensive pollution index evaluation table

Site	P_i					Pc	Level
	Mn	Cu	Pb	Cd	Zn		
Niubahuang	/	7.09	14.51	24.14	5.03	19.29	Heavy pollution
Laochang	/	6.01	12.51	34.24	3.67	26.19	Heavy pollution
Kafang	/	3.93	14.77	15.84	5.25	13.23	Heavy Pollution
Southern	/	3.71	14.63	11.10	3.22	11.85	Heavy pollution
Mean value		5.19	14.11	21.33	4.29	17.64	Heavy Pollution
Class III	/	400.00	500.00	1.00	500.0		

Heavy metal content in mine tailing

The statistical analysis of soil heavy metal content in the sites are shown in table 7: The average content of five different kinds of heavy metals (Mn, Cu, Pb, Cd, Zn) are respectively: 5700.9897 mg/kg, 2041.1963 mg/kg, 7164.7249 mg/kg, 21.3295 mg/kg and 2146.8060 mg/kg. The order based on the average content is: Pb > Mn > Zn > Cu > Cd. With reference to the state soil environment quality standard (GB15618-1995), the content of Cu, Pb, Cd and Zn are 40.82 times, 28.66 times, 71.09 times and 10.73 times respectively more than the 2nd class standard while Cu, Pb, Cd and Zn also goes beyond level three based on the soil environment quality standard, and 5.10 times, 14.33 times, 21.33 times and 4.29 times respectively. Therefore, it can be initially determined that in the mine tailings of Gejiu, Cd pollution is the most serious. In addition, the content of Mn in all kinds of soils is relatively high, this may be related to the background value of soil itself.

Assessment of the heavy metal pollution of wasteland soil index

Assessment of soil pollution based on single contamination and Nemero comprehensive pollution index

The national soil environmental quality standard is used in this paper to give an assessment of the pollution by heavy metals(Mn, Cu, Pb, Cd, Zn) in tin mine tailings with single contamination pollution index and Nemero comprehensive pollution index. Due to no any limitation on Mn element in view of the national soil environmental quality standard, so the evaluation on pollution only made for the other four elements in the study , the results as shown in table 8. It Can be seen from the single contamination pollution index, the heavy metal Cu, Pb, Cd and Zn in the different site the average value of their single contamination pollution index is 5.19, 14.11, 21.33 and 5.19, respectively. Among which Cd pollution in Laochang is the most serious with pollution index up to 34.24. Therefore, Cd is the main pollution contamination in the wasteland. According to the national soil environmental quality standard, all sites are heavy pollution. Compared with single contamination pollution index, multi-contamination comprehensive evaluation results of pollution index is different, which shows the effect of contamination with high concentration on soil environmental quality and the range between 11.85 ~ 26.19, with mean value of 17.64, the comprehensive pollution index is greater than three and are heavy pollution according to the national soil environmental quality standard.

Assessment of soil pollution based on geoaccumulation index

The impacts from heavy metals on the environment caused by natural and human activities is considered by Geoccumulation index, also the changes of background value might be caused by natural diagenesis. Therefore, in this paper, soil environmental background value of Yunnan province was taken as the evaluation standard. The table 9 shows that based on the soil environmental background value in Yunnan province and the geoaccumulation index, the pollution of Mn in soil surface ranks at grade III in the four sites, and the pollution degree is at moderate level; Cu, Pb, Cd pollution are at grade VI and the pollution is very serious pollution; Zn pollution is at 4 ~ 5, pollution is extremely serious pollution. In addition to Mn for middle level pollution in the abandoned land, the heavy metal element of Cu, Pb, Cd, and Zn are extremely serious pollution to the land. According to the mean value of I_{geo}, the order for the pollution degree by the heavy metal elements: the Cd > Pb > Cu > Zn > Mn, Cd and Pb are extremely serious pollution and the main contamination in the sites.

Assessment of soil pollution based on geoaccumulation index

Potential ecological risk index (E_r^i) of single heavy metal in the four sites and the potential ecological risk index (RI) of the five different heavy metals, as well as the reference value based on the environmental background value of Yunnan are shown in table 10 refs. The table 10 shows that the order for the potential ecological risk index(E_r^i) of five heavy metal elements according to the average size in the order: Cd > Pb > Cu > Zn > Mn. Among them, there is no big difference for the potential ecological risk index of Mn in the four sites and is between 10.51 ~ 10.51, with a mean value of 11.07; The potential ecological risk index of Cu ranging between 258.86 ~ 494.10; the potential ecological risk index of Pb between 875.89 ~ 1016.37; The potential ecological risk index of Cd range is 4012.63 ~ 12374.49; the potential ecological risk index of Zn in the range of 18.74 ~ 30.54. According to Hankanson potential ecological risk assessment standard, Cu, Pb and Cd in the four sites are extreme heavy ecological risk(E_r^i≥320); Mn and Zn are mild ecological risk (E_r^i< 40). Based on the potential ecological risk index (RI) of various of heavy metals, the ecological risks are extremely heavy in the four sites (RI≥ 600), this is because the risk index of Cu, Pb and Cd is bigger than the others, and the result is consistent with the comprehensive pollution index assessment.

Table9 The geoaccumulation index of heavy metal of wasteland soil

site	I_{geo}									
	Mn	**Index class**	**Cu**	**Index class**	**Pb**	**Index class**	**Cd**	**Index class**	**Zn**	**Index class**
Niubahuang	2.98	3	6.04	6	7.08	6	7.60	6	4.28	5
Laochang	2.88	3	5.80	6	6.87	6	8.10	6	3.83	4
Kafang	2.81	3	5.19	6	7.19	6	6.99	6	4.45	5
Southern	2.88	3	5.11	6	7.09	6	6.48	6	3.64	4
Mean value	2.88	3	5.54	6	7.06	6	7.29	6	4.05	5
Soil environment background value of YN(mg/kg)	515		28.7		35.7		0.083		86	

Table10 The potential ecological risk index (E_r^i) and potential ecological risk index (RI) of heavy metals of wasteland soil

site	E_r^i					RI	Potential ecological
	Mn	Cu	Pb	Cd	Zn		
Niubahuang	11.83	494.10	1016.37	8725.84	29.24	10277.	Extreme
Laochang	10.88	418.51	875.89	12374.49	21.34	13701.	Extreme
Kafang	10.51	273.94	1097.04	5312.64	30.54	6724.6	Extreme
Southern	11.07	258.86	1024.58	4012.63	18.74	5325.8	Extreme
E_r^i mean value	11.07	361.35	1367.33	7606.4	24.97		
Pollution degree	Mild	Very	Extreme	Extreme	Mild		
Soil environment background value of	515	28.7	35.7	0.083	86.0		

CONCLUSION AND SUGGESTION

a. All the organic soil fertility index level mostly at VI level while the soil fertility for other elements such as total N, total P, effective P and total K such as effective P at the level between III ~ VI basically, soil fertility of available K at level II mostly.Tthe soil fertility size order: Laochang > Kafang > Southern >Niubahuang.

b. The average content of five different heavy metals (Mn, Cu, Pb, Cd, Zn) is 5700.9897 mg/kg, 2041.1963 mg/kg, 7164.7249 mg/kg, 21.3295 mg/kg and 2146.8060 mg/kg respectively. According to the size the order is: Pb > Mn > Zn > Cu > Cd. With reference to the State Soil Environment Quality Standard (GB15618-1995), the content of Cu, Pb, Cd and Zn are 40.82 times, 28.66 times, 71.09 times and 10.73 times than that of the 2nd class while Cu, Pb, Cd and Zn and also goes beyond the soil environment quality level 3 standard and 5.10 times, 14.3 times than that.

c. The choice of evaluation method for the assessment on soil pollution is very important, different method reflects the different results. The results shows the pollution is heavy by using the single contamination pollution index method and Nemero comprehensive pollution index method; And it shows that Mn and Zn are mild ecological risks while Cu, Pb and Cd are extreme heavy with Hankanson potential ecological risk index; Geoaccumulation index evaluation results show that Mn pollution is for level 3, Cu, Pb, Cd pollution at level 6, the pollution of Zn level between 4 ~ 5. However the four evaluation methods are based on the total amount of heavy metals as an index to evaluate without taking into account geometrical shape of heavy metals in soil. In fact, the heavy metals in soil exist in many forms, different forms of the element may have different toxicity (). Some references show that it is impossible to make precise prediction assessment of heavy metal pollution degree and soil heavy metal biological effectiveness () only on the basis of the total amount of soil heavy metals. So it is necessary to carry out further study in the region later on.

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