ISSN : 0974 - 7435 Volume 10 Issue 6

BioTechnology

An Indian Journal

FULL PAPER

BTAIJ, 10(6), 2014 [1660-1665]

Heavy metal pollution and ecological risk assessment of soils from ancient Linglong gold mine area, China

Lei Zhang*

College of Resource and Environment, Qingdao Agricultural University, Qingdao, 266109 (CHINA)

E-mail:zhanglei_lw@163.com

ABSTRACT

Linglong gold-mining area has a history of mining for over 1000 years. To understand the effect on heavy metal accumulation in soil by gold mining and smelting for a long term, the contents and the potential ecological risks of heavy metals in Linglong gold mine area were studied. The content range of Hg and Cd in soil varied respectively from 0.094-4.04 mg/kg and 0.03-2.23 mg/kg. The corresponding average value was 0.36 mg/kg and 0.30 mg/kg. The average Pb and Cr content was 64.37 mg/kg and 23.23 mg/kg. Compared with Chinese Soil Reference (Grade II), the over standard rate of Hg and Cd was 50.0% and 26.1%, respectively. The geoaccumulation index evaluation presented that Hg and Cd in soil demonstrated a comparatively high level of accumulation characteristics. Medium or severe contamination was detected in most sample points. Cd content in soil was positively proportional to clay particles. The potential ecological risk assessment presented that the average ecological risk index of Hg and Cd was 344.3 and 221.9 respectively, indicating remarkable ecological risk. The average comprehensive risk index of heavy metal pollutant reached 632.2, showing significant comprehensive ecological risk of heavy metal pollutant.

KEYWORDS

Heavy metals;
Soil properties;
Potential ecological risk;
Gold mining.

INTRODUCTION

Heavy metal pollution in soil not only seriously affects and changes the ecosystem function of soil, but also jeopardizes quality of agricultural products and threats to human health. The elusiveness and toxicity of heavy metal pollutant in soil makes this an important focus in the current research field of environmental science[1,2]. At present, all over the globe, studies on heavy metal pollution in soil mainly concentrate on the investigation of sources, pollution evaluation, ecological risk assessment, effects on human health as well as pollution remediation[3-5]. In China, sewage irrigation, sludge utilization, mining and smelting are the main sources of heavy metals in soil[6]. The mining and smelting operations harm the surface ecosystems of the mining field. Besides, their emissions, wastewater discharges and waste stocking also produce serious heavy metal pollution to the soils of mining area.

Zhaoyuan City of Shandong Province is a renowned "City of Gold" in China. It is of great importance in terms of gold yield, the geological and mineralization rules of gold mines. Zhaoyuan now owns over 20 gold mines of different scales. Among them, Linglong gold-mining area is one of the oldest gold mines, with a history of mining for over 1000 years. To understand the effect of gold mining and smelting for a long term, we investigated the contents and distribution of heavy metal in soil in Linglong Gold Field, as well as their relationship with the physical and chemical properties of soil. On this basis, potential ecological risks of heavy metal in soils from the gold field were also evaluated, with the aim to provide basis for heavy metal pollution remediation in mining area as well as the safety of agricultural products.

METHODS

Sample collection

In May 2010, soil samples were collected from Linglong gold mining area. The layout of sampling points was arranged by the grid method and a total of 46 soil samples were collected. Each sample was treated by multipoint mixing method. Every 6 to 7 surface soil samples (0-20 cm) were mixed in to one final sample. Soil samples were air-dried, ground and sieved through 2 mm mesh for determining physical and chemical properties. The plastic or wooden tools were used in sampling process to avoid pollution of metals. A part of each sample was ground and passed through a 0.149 mm nylon sieve for analysis of total concentrations of mercury (Hg), cadmium (Cd), lead (Pb) and chromium (Cr).

Sample analysis and quality assurance

Soil chemical properties were measured using routine method. After digested in mixture of HNO_3-HF-$HClO_4$, the concentrations of Cd, Pb and Cr in soils were determined by AAS (AA-7000, Shimadzu, Japan). Hg content was determined by H_2SO_4-HNO_3-V_2O_5 digestion method and measured by cold vapor atomic absorption spectrometry (CVAAS) (F732-V, Huaguang, China). Glass apparatus used for sample analysis were immersed in 15% nitric acid (v/v) for 24 h, then thoroughly washed with deionized water before use. Certified standard soil samples GBW07401 (GSS-1) were used to ensure precision of the measurement.

Evaluation methodology

Geoaccumulation index

Geoaccumulation index method was proposed by Muller[7]. This method reflects the intuitive pollution level of heavy metal pollutants as well as the accumulation degree of heavy metal pollutants in soils/sediments. Currently, it is widely used in the research field of evaluating heavy metal pollution in soil. The equation is as follows:

$$I_{geo}=\log_2[C_i(k\times B_i)]$$

I_{geo} is the geoaccumulation index; C_i is the concentration of evaluation element i in soil; B_i is the background value of i; k is generally taken as 1.5, which is a correction factor to eliminate possible background value variation caused by rock differences in various areas. Forstner et al. divided the geoaccumulation index into 7 levels[8]. Different levels represent different degrees of pollution.

Potential ecological risk index method

Potential ecological risk index method was established by Hakanson using principles of sedimentology to evaluate heavy metal pollution and potential ecological risks[9]. This method reflects not only the impact of different pollutants in a certain circumstance, but also the comprehensive influence of various pollutants. It can quantitatively identify the degree of potential ecological risks of heavy metal pollutant, and is considered as the most widely used method to evaluate potential ecological risks of heavy metal pollutants. The computational formula is as follows:

$$C^i_f = C^i / C^i_n ;\ E^i_r = T^i_r \times C^i_f$$

$$RI=\sum_{i=1}^{n}E_r^i=\sum_{i=1}^{n}T_r^i\times C_f^i$$

C^i_f is the pollution coefficient of the i-*th* heavy metal pollutant; C^i is the measured value of the i-*th* heavy metal pollutant content among samples (mg/kg); C^i_n is the background value of the i-*th* heavy metal pollutant (mg/kg); E^i_r is the potential ecological risk coefficient of the i-*th* heavy metal pollutant; T^i_r is the toxicity coefficient of the i-*th* heavy metal pollutant, reflecting the toxicity levels and biological sensitivity of the pollution; RI is the combined potential ecological risk index of various heavy metal pollutants. In our research, the background value of brown soil area in Shandong Peninsula was taken as the reference. The standard toxicity coefficient of heavy metal established by Hakanson (T^i_r) was: Cr (2) <Pb (5) <Cd (30) <Hg (40). The classi-

fication criteria of ecological risk index and ecological risk index of metal pollution are shown in TABLE 1.

RESULTS AND DISCUSSIONS

Heavy metal contents

In Linglong gold mine area, Pb and Cr content in soil was normally distributed. The skewed distribution of Hg and Cd content was observed. After the logarithmic conversion, Hg and Cd content was in line with normal distribution. Hg and Cd content among heavy metal pollutants presented great dispersion, and the content range of Hg and Cd was 0.094-4.04 mg/kg and 0.03-2.23 mg/kg respectively. The geometric mean of Hg and Cd was 0.36 mg/kg and 0.30 mg/kg. The dispersion degree of Pb and Cr content was smaller and their arithmetic mean was 64.37 mg/kg and 23.23 mg/kg respectively (TABLE 2). Compared with local background contents of metals[10], Hg and Pb content of all sample points exceeded the background value. The exceeding median point of Cd content reached 97.2%, showing the pollution status. According to Chinese Soil Reference (Grade II), the exceeding rate of Hg and Cd was 50.0% and 26.1% respectively, indicating that the gold mining and smelting have caused serious heavy metal pollution of the local farmland soil.

The correlation analysis was carried out between heavy metal pollutant content and soil properties of soil at different sample points (TABLE 3). There was an extremely significant positive correlation between Hg and Cr, and between Pb and Cd ($p<0.01$), indicating the possible homology of different heavy metal pollutants. Tailing stocking, leaching and dispersion of pollutants, waste water, dust spreading of exhaust gas emissions will influence the content and distribution of heavy metal in surface soils. Cd content in soil was significantly positively correlated with the proportion of clay particles (particle size < 0.002mm). Besides, cation exchange capacity (CEC) was significantly positively correlated with organic matter content. Pb showed extremely significant negative correlation with CEC. Cr was significantly and positively correlated with the proportion of coarse soil particles (0.02-1 mm). Compared with other metal elements, Cd tends to migrate in soil. Meanwhile, its combination with organic matter and fine particles can retain more Cd elements in the surface layer of soil, leading to the increase of Cd content[11,12].

TABLE 1 : The classification of assessment index of potential ecological risk levels

Level of risk	A	B	C	D	E
E^i_r	?40	40-80	80-160	160-320	>320
RI	?150	150-300	300-600	>600	
Degree of ecological risk	Slight	Medium	Strong	Severe	Extremely severe

TABLE 2 : Statistical characteristics of heavy metals in study areas

	Range (mg/kg)	Geometric mean(mg/kg)	Median (mg/kg)	Arithmetic mean (mg/kg)	SD (mg/kg)	CV	Exceeding rate(%)	
							Background value	Soil Quality Standard (Grade II)
Hg	0.09-4.04	0.36	0.31	0.56	0.69	1.22	100	50
Cd	0.03-2.23	0.30	0.28	0.41	0.41	1.00	97.2	26.1
Pb	36.36-170.24	59.33	56.61	64.37	31.94	0.50	100	0
Cr	7.54-52.27	21.88	21.68	23.23	8.83	0.38	17.4	0

TABLE 3 : Correlation analysis between contents of metals and soil properties

	Hg	Cd	Pb	Cr	pH	CEC	OM	P1(1-0.02 mm)	P2 (0.02-0.002 mm)	P3 (<0.002 mm)
Hg	1	0.042	0.085	0.322**	-0.069	0.141	0.018	0.005	0.129	-0.114
Cd		1	0.529**	0.019	0.154	0.379**	0.227*	0.128	-0.059	0.420**
Pb			1	-0.295*	-0.022	0.331**	0.133	-0.082	0.238*	0.026
Cr				1	0.029	-0.128	-0.015	0.295*	-0.040	-0.135

Cr in soil was less affected by external pollutions and more possibly originated from the soil parent material.

Geoaccumulation index evaluation

To evaluate the accumulation of heavy metal in soil in Linglong Gold Field, the background values of elements in brown soil area of Shandong Province were referred to calculate the geoaccumulation index(I_{geo}). The calculation results are shown in TABLE 4. The geoaccumulation index grade of Cd in soil samples varied between Grade 0 and 6. In other words, it was distributed from the pollution-free area to severely polluted areas. The amount of the the geoaccumulation index of Cd >1-2 and that >2-3 was 14 and 19 respectively, accounting for 30.4% and 41.3% of all samples. This indicated that Cd in soil was mainly distributed in medium pollution and medium-severe pollution areas. The geoaccumulation indexes of Hg were mainly distributed in areas with at least medium pollution, which accounted for 84.8% of all sample points. The indexes in areas above severe pollution still accounted for 30.4%, which indicated extremely serious Hg and Cd pollution in soil of the research area. The geoaccumulation indexes of Pb in medium pollution areas accounted for 82.6% of all sample points. Compared with other heavy metal pollutant elements, Cr did not present any tendency of pollution.

Previous studies have shown that in the alchemical process of amalgamation, for every 1 g of gold produced, 1.2-1.5 g of mercury was discharged into the environment. The mercury in the tailings accumulated on the ground surface via processes like leaching, percolation, volatilization and deposition. The mercury may exist for thousands of years, leading to horrible mercury pollution of soil, sediments and water in the gold field[13,14]. In 1996, China quit the practice of amalgam treatment for gold metallurgy. However, the previous gold metallurgy based on indigenous methods has released a certain amount of mercury into the environment, which may exist for a long term. This has produced serious mercury pollution in gold fields. Cd concomitant in ores may be a key reason for Cd accumulation in soil.

TABLE 4 : Distribution and classification of geoaccumulation index for soils samples

Grade	Pollution level	Geoaccumulation Index (I_{geo})	Number of samples			
			Hg	Cd	Pb	Cr
0	No pollution	≤0	0	1	0	44
1	Light	0~1	7	2	3	2
2	Medium	>1~2	9	14	38	0
3	Median-severe	>2~3	16	19	4	0
4	Severe	>3~4	8	6	1	0
5	Severe-extreme	>4~5	4	3	0	0
6	Extreme	>5	2	1	0	0

Potential ecological risk assessment of heavy metal in soil

Based on potential ecological risk index (E^i_r) of a single metal element (TABLE 5), the scope of changes in the ecological risk index of Hg and Cd was large and the average value was 344.3 and 221.9 respectively, showing extremely strong and very strong ecological risks. The ecological risk of Pb and Cr was comparatively small, which was respectively slight and medium. The comprehensive risk index of heavy metal pollutants in the research area varied from 132.7 to 5747.5, and the average risk index was 632.2, showing strong comprehensive ecological risks of heavy metal pollutants (TABLE 5).

According to the distribution of potential ecological risk coefficient of various sample points in the research area (Figure 1), Pb and Cr was mainly distributed in the range of 0-40, which accounted for 90.2% and 100% of all sample points. Meanwhile, Hg was mainly distributed in the range >160, accounting for 78.2% of all samples. The ecological risk index of Cd was mainly distributed in the range of 80-320, accounting for 71.7% of sample points. This indicated that in all the soil of Linglong gold mining area, heavy metal pollutant Hg and Cd presented intensive potential ecological risks. According to the comprehensive ecological

TABLE 5 : Statistics of potential ecological risk index and comprehensive risk index of heavy metals in study area

	Potential ecological risk index (E_r^i)				Comprehensive risk index (RI)
	Hg	Cd	Pb	Cr	
Maximum	83.2	22.3	13.6	13.6	132.7
Minimum	3847.4	1742.5	63.5	94.1	5747.5
Average	344.3	221.9	24.0	42.0	632.2
SD	652.5	306.6	11.9	15.9	986.9

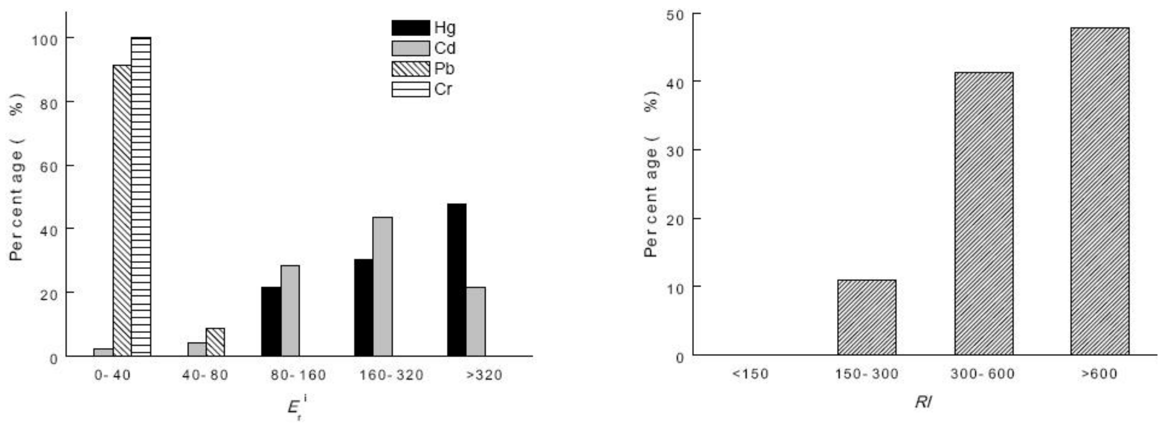

Figure 1: Distribution of potential ecological risk index (E_r^i) and comprehensive risk index (RI) of heavy metals in study Area

risks, in all samples, the amount of indexes in the strong risk range between 300 and 600 accounted for 41.3% of all samples. That >600 took up for 47.8%. This presented that long-term gold mining and smelting and other human activities have caused serious heavy metal pollution to the surface soil of the mining field. It presented significant potential ecological risks. The research results demonstrated that further measures should be taken to restore the heavy metal pollution in Linglong gold mining area, and to prevent the migration of heavy metal pollutants to the food chain in the agricultural utilization.

CONCLUSION

The range of Hg and Cd content in the soil of Linglong gold mining area was 0.094-4.04 mg/kg and 0.03-2.23 mg/kg respectively. The average Hg and Cd content was 0.36 mg/kg and 0.30 mg/kg. The average Pb and Cr content was 64.37 mg/kg and 23.23 mg/kg. Compared with Chinese Soil Reference (Grade II), the exceeding rate of Hg and Cd was 50.0% and 26.1%. The geoaccumulation index evaluation presented that Cd elements in soil were distributed mainly in medium and medium-severe pollution areas. Among all samples, 84.8% of the geoaccumulation indexes of Hg were mainly distributed in areas above medium pollutions. It indicated extremely serious Hg and Cd pollution in soil of the research area. The average value of the ecological risk index of Hg and Cd was 344.3 and 221.9 respectively, indicating extremely strong and very strong ecological risks. The comprehensive risk index of heavy metal pollutants in the research area varied from 132.7 to 5747.5, and the average risk index was 632.2, showing strong comprehensive ecological risks of heavy metal pollutants.

ACKNOWLEDGMENT

This research is supported by the Natural Sciences Foundation of Shandong Province (No. 2009ZRB019E5) and National Natural Science Foundation of China (No. 41101472, 41101094).

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