Asian Agricultural Research 2015, 7(9): 54 –57

Evaluation on Soil Heavy Metal Pollution around Tailing Areas: A Case Study of Ag-Sb Deposit in Northeastern Guangdong

Deliang LIU[1*], Kaifeng WANG[2], Qihe YANG[1], Qin Zhu[1]

1. School of Life Sciences, Jiaying University, Meizhou 514015, China; 2. School of Chemistry and Environment Sciences, Jiaying University, Meizhou 514015, China

Abstract In October 2012, an evaluation using potential ecological hazard risk index was carried out on soil heavy metal pollution around Ag-Sb deposit tailing areas in northeastern Guangdong. Results indicate that (i) soil heavy metal pollution is mainly Cd-Ni compound pollution, including Cd content 0.31 –2.66mg/kg (average content is 1.11 mg/kg), the situation of exceeding standard is serious (the rate of exceeding standard is 100%); the total potential ecological hazard risk index (RI) is between 50 and 300, and it is moderate pollution; (ii) in soil heavy metal content, only Ni and Cu are positively correlated. Since there is certain degree of Ni pollution in this deposit, the synergetic effect of Cu and Ni may deteriorate Ni pollution.

Key words Ag-Sb deposit in northeastern Guangdong, Heavy metals, Soil pollution, Evaluation, Correlation

Heavy metals are metals with atomic weight higher than 40 and specific density greater than 4 or 5. Many heavy metals are trace elements having important function for plant nutrition. Physiological functions of these elements depend on their concentration. At low concentration, elements may be essential elements for living of organisms, but they may be passively absorbed and do not generate physiological function; at high concentration, they will generate toxic function to organisms. Therefore, they are often considered as toxic elements, namely, heavy metal pollution. These heavy metals include Cu, Zn, Cd, Pb, Hg, Cr, As, Ni, and Co, etc[1,2]. Heavy metals are easily accumulated in soil but difficultly to be decomposed by soil microorganism. This not only influences physical and chemical properties of soil, impedes effective supply of nutrients, restricts growth and development of plant, but also may be changed into methyl chemicals, and ultimately threatens people's health through transfer of biological chain and food chain[3,4].

Meizhou in eastern Guangdong is rich in mineral resources. There are 48 proven minerals, including coal, iron, copper, manganese, lead, zinc, silver, antimony, rare earth, limestone, granite, marble, and 530 deposits. In more than 10 years of mining, solid wastes of mines, such as open-cast, waste dump, tailing areas, and subsidence areas are major sources of soil heavy metal pollution[5]. For this, we took Ag-Sb deposit tailing areas in northeastern Guangdong as study object, and evaluated content of heavy metals (Zn, Cu, Ni, Cd and Cr) and their pollution in Ag-Sb deposit tailing areas in northeastern Guangdong, in the hope of providing reference for land reclamation and ecological restoration of this mining area.

1 Materials and methods

1.1 Collection of soil samples In October 2012, considering specific terrain and hydrological conditions of this tailing area stockpiling, we set sample collection points in hillside along sewage discharge ditches and two sides. In 1km range, we set 16 sampling points in different function areas (slag area, wild forest land, paddy field, non-irrigated farmland (peanut land and corn land)), 16 sampling points in orchards, including 3 in slag land, 3 in wild forest land, 2 in paddy field, 4 in non-irrigated land, and 4 in orchard, as listed in Table 1. Sampling depth is 0 –15 topsoil. In 1 × 1m^2 sampling area of each sampling point, we collected 5 –10 sub-samples to form a mixed soil sample.

Table 1 Generation situation of sampling points

No.	Longitude and latitude	Description	Distance m
1	N24°31.182′, E116°16.813′	Slag No.1	333
2	N24°31.182′, E116°16.813′	Slag No.2	416
3	N24°31.308′, E116°16.955′	Slag No.3	450
4	N24°31.307′, E116°17.018′	Wild forest land No.1	448
5	N24°31.304′, E116°17.045′	Wild forest land No.2	371
6	N24°31.279′, E116°17.057′	Wild forest land No.3	284
7	N24°31.312′, E116°16.981′	Paddy field No. 1	768
8	N24°31.335′, E116°16.824′	Peanut land No.1	742
9	N24°31.574′, E116°16.961′	Corn land No.1	576
10	N24°31.560′, E116°16.959′	Paddy field No. 2 (upstream)	623
11	N24°31.485′, E116°16.889′	Peanut land No. 2 (upstream)	643
12	N24°31.518′, E116°16.826′	Honey pomelo land No.1	622
13	N24°31.528′, E116°16.780′	Peanut land No.3	649
14	N24°31.505′, E116°16.912′	Honey pomelo land No.2	649
15	N24°31.518′, E116°16.922′	Citrus grandis land No.1	823
16	N24°31.577′, E116°17.036′	Honey pomelo land No.3	912

Received: May 26, 2015 Accepted: July 25, 2015
Supported by Science and Technology Planning Project of Guangdong Province (2012A030700006); Key Sci-tech Innovation Project for Institutions of Higher Education in Guangdong Province (cxzd 1132), Joint Natural Science Project of Meizhou and Jiaying University (2011KJM08).
* Corresponding author. E-mail: ldl@jyu.edu.cn

1.2 Sample processing and test

1.2.1 Preprocessing of samples. Put collected samples in shady and cool place for 12 – 13 days. After naturally dry, using quartering, we took about 2 kg samples, ground proper soil samples in agate mortar, prepared samples in 20 mesh (bore diameter 0.84 mm), 80 mesh (bore diameter 0.200 mm), and 120 mesh (bore diameter 0.133 mm), and placed samples in bake oven to dry for 24 hours for use.

1.2.2 Measurement of samples. After samples were digested in mixed acid $HCl - HNO_3 - HF - HClO_4$, we measured concentration of heavy metals Zn, Cu, Ni, Cd, and Cr by atomic absorption spectrometry (Shimadzu atomic absorption spectrophotometer AA – 6300 (P/N 206 – 51800)), and repeated three times of test.

1.3 Evaluation methods

1.3.1 Single factor pollution index method of heavy metals. We made single factor pollution evaluation of heavy metals using the following calculation formula[6]:

$$P_i = C_i / S_i \qquad (1)$$

where P_i denotes single factor pollution index of the i-th heavy metal in soil; C_i is measured content of the i-th heavy metal in soil; S_i is evaluation standard of the i-th heavy metal. We adopted Grade II Criteria of the *Standard for Soil Environmental Quality in GB*15618 – 1995[7].

In general, the higher P_i means the higher pollution. $P_i \leqslant 1$: not polluted; $1 < P_i \leqslant 2$: mildly polluted; $2 < P_i \leqslant 3$: moderately polluted; $P_i > 3$: seriously polluted.

Table 2 Toxic coefficient of soil heavy metals

Metal elements	Ni	Zn	Cr	Cd	Cu
Toxic response factor	5	1	2	30	5

1.3.2 Ecological hazard index evaluation method. The potential ecological hazard index method is an influential method widely applied in the world[8, 9]. According to researches of Swedish scholar Hakanson, the potential ecological hazard coefficient Ei of the i-th heavy metal of single heavy metal in soil can be denoted as:

$$E_i = T_i \times P_i \qquad (2)$$

where T_i is the toxic coefficient of the heavy metal i[10], as indicated in Table 2; P_i is single pollution index of the i-th metal in soil.

The potential ecological hazard coefficient (E_i) describes the pollution degree of a certain pollutant (element), while potential ecological hazard index (Table 3) describes the overall value of potential ecological hazard coefficient in certain point, namely, the potential ecological hazard risk index (RI) of many heavy metals in soil is the sum of potential ecological hazard coefficient (E_i) of single heavy metals:

$$RI = \sum_{i}^{n} E_i \qquad (3)$$

Table 3 The relation between potential ecological hazard coefficient and pollution degree of heavy metals

	Grades of pollution degree				
E_i	<40	$40 \leqslant E_i < 80$	$80 \leqslant E_i < 160$	$160 \leqslant E_i < 320$	$E_i \geqslant 320$
RI	<50	$50 \leqslant RI < 300$	$300 \leqslant RI < 600$	$RI \geqslant 600$	$RI \geqslant 600$
Pollution degree	Low	General	Medium	High	Higher

Table 4 Content of heavy metals in soil//mg/kg

Heavy metal	Min.	Max.	Average value	Standard deviation	GB15618 – 1995 Grade II standard
Zn	49.10	448.20	153.00	97.0	200.00
Cu	14.50	108.30	35.30	28.3	50.0
Ni	51.20	206.10	92.90	45.5	40.0
Cd	0.31	2.66	1.11	6.4	0.3
Cr	28.70	361.20	178.80	103.1	250.0

2 Results and analyses

2.1 Heavy metals in soil With reference to grade II standard in *Standard for Soil Environmental Quality* in GB15618 – 1995, from Table 5, we know that Cd and Ni exceed the standard, the average value of Cd (1.11 mg/kg) reaches 4 times the standard, the maximum value exceeds 9 times, average value of Ni (92.9 mg/kg) exceeds one time the standard, and the maximum standard exceeds 5 times. The standard deviation indicates that there is a high difference in heavy metal content in sample points. Therefore, to evaluate actual level and degree of heavy metal pollution, it is necessary to make evaluation of different sampling points and their function areas.

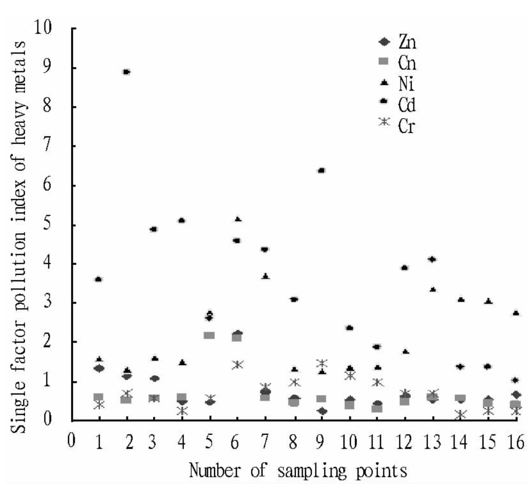

Fig. 1 The evaluation results of single factor pollution

2.2 Evaluation of heavy metal pollution

2.2.1 Analysis of single factor pollution index of heavy metals. From Fig. 1 and Table 5, there is a sharp difference (1.03 – 8.87) in P_i of soil heavy metal Cd in all sampling points. Sampling point No. 2 has the highest P_i (8.87), and sampling point

No. 16 has the lowest P_i (1.03), the rate of exceeding standard is 100%, number of heavy metal polluted points ($P_i > 3$) is 10 and the percentage is 62.50%. Variance analysis indicates that the P_i difference of heavy metal Cd reaches the extremely significant level ($P < 0.01$). Through Q test, as per $L.S.D = Q_{0.01}(s^2/n)^{1/2}$, we obtained the minimum significance difference is 3.54. With distance increase of original ore processing shop, especially slag piling place, Cd value drops accordingly. Generally, change trend of heavy metal Cd in soil of different sampling points in different function areas is as follows: slag area, forest land, paddy field, non-irrigated farmland (peanut land and corn land), and orchard.

From Fig. 1 and Table 5, there is a sharp difference (1.28 – 5.15) in P_i of soil heavy metal Ni in all sampling points. Sampling point No. 6 has the highest P_i (5.15), and sampling point No. 9 has the lowest P_i (1.28), the rate of exceeding standard is 100%, number of heavy metal polluted points ($P_i > 3$) is 5 and the percentage is 31.25%. Variance decomposition analysis indicates that the P_i difference of soil heavy metal in sampling points reaches significant level ($P < 0.05$), but change trend of Ni in different functions is not obvious. Other heavy metals such as Zn, Cu, and Cr have certain difference in P_i, but there is no sampling point seriously polluted ($P_i > 3$), and the pollution is relatively mild.

Table 5 Single factor pollution evaluation results of heavy metals

Heavy metals	Number of sampling points	Evaluation index P_i range	Pollution index P_i								Rate of exceeding standard // %
			$P_i \leq 1$ (not polluted)		$1 < P_i \leq 2$ (mildly polluted)		$2 < P_i \leq 3$ (moderately polluted)		$P_i > 3$ (seriously polluted)		
			Q'ty	%	Q'ty	%	Q'ty	%	Q'ty	%	
Zn	16	0.25 – 2.24	12	75.00	3	18.75	1	6.25	0	0.00	25.00
Cu	16	0.29 – 2.17	14	87.50	0	0.00	2	12.50	0	0.00	12.50
Ni	16	1.29 – 5.15	0	0.00	9	56.25	2	12.50	5	31.25	100.00
Cd	16	1.03 – 8.87	0	0.00	4	25.00	2	12.50	10	62.50	100.00
Cr	16	0.15 – 1.45	13	81.25	3	18.75	0	0.00	0	0.00	18.75

2.2.2 Potential ecological hazard risk index. From the single factor potential ecological hazard coefficient E_i (Table 6), among 16 sampling points surveyed, 2 sampling points have high Cd pollution ($160 \leq E_i < 320$), sampling point No. 2 (265.99) and sampling point No. 9 (190.82); 8 sampling points have higher Cd pollution ($80 \leq E_i < 160$); 5 sampling points have medium Cd pollution ($40 \leq E_i < 80$); and one sampling point have low Cd pollution ($E_i < 40$). Other four heavy metals Zn, Cu, Ni and Cr are at low pollution level ($E_i < 40$).

Table 3 The potential ecological hazard coefficient (Ei) and risk index (RI) of heavy metals in soil

No. of sampling point	E_i					RI
	Zn	Cu	Ni	Cd	Cr	
1	1.33	3.00	7.90	108.44	0.83	121.50
2	1.14	2.51	6.45	265.99	1.41	277.50
3	1.08	2.86	8.15	145.82	1.18	159.09
4	0.52	3.00	7.56	152.79	0.52	164.39
5	0.49	10.83	13.84	78.22	1.18	104.56
6	2.24	10.51	25.77	138.15	2.89	179.56
7	0.72	2.92	18.53	130.68	1.71	154.56
8	0.58	2.23	6.73	93.20	2.00	104.74
9	0.25	2.75	6.40	190.82	2.89	203.11
10	0.55	1.87	6.82	70.69	2.30	104.74
11	0.44	1.45	7.06	55.65	2.00	203.11
12	0.63	2.40	8.92	115.64	1.41	82.23
13	0.54	3.09	16.84	123.16	1.41	66.60
14	0.55	2.84	15.68	40.59	0.23	129.00
15	0.54	2.23	15.24	40.59	0.53	145.04
16	0.67	2.06	13.83	30.61	0.53	59.89

From total potential ecological hazard risk index (RI), as listed in Table 7, RI of all sampling points is in the range of $50 \leq RI < 300$ and belongs to the medium pollution level. This is possibly because Cd pollution and pollution degree in sampling points are different. In general, RI change trend is slag land > forest land > paddy field > non-irrigated farmland > orchard.

2.3 Correlation analysis of soil heavy metal pollution

From Table 7, we know that there is different level of correlation between heavy metals in soil, but only Ni and Cu reach the significant level of correlation. It should be noted that because there is certain level of Ni pollution in this tailing area, the synergetic effect of Cu and Ni may deteriorate Ni pollution.

In addition, from the perspective of the distance from sampling points to original ore processing shops, there is significantly negative correlation between heavy metal Cd, Zn and Cu and the distance, indicating that soil heavy metals fall with the increase in distance to the ore separation processing shop. Therefore, in agricultural and forestry production, to guarantee ecological security of foods, it is not appropriate to carry out production activities near the ore processing shops and slag stockpiling areas.

Table 7 Correlation of content of heavy metals in soil

	Distance // m	Zn	Cu	Ni	Cd	Cr
Distance // m	1.00					
Zn	–0.58*	1.00				
Cu	–0.59*	0.48	1.00			
Ni	0.02	0.46	0.58*	1.00		
Cd	–0.55*	0.28	0.06	–0.23	1.00	
Cr	–0.20	0.22	0.22	0.02	0.36	1.00

Note: * denotes significant correlation.

3 Conclusions

Firstly, soil heavy metal pollution is mainly Cd – Ni compound pollution, including Cd content 0.31 – 2.66 mg/kg (average content is 1.11 mg/kg), and Ni content 51.2 – 92.9 mg/kg (average content is 92.9 mg/kg). From the single factor potential ecological hazard coefficient Ei (Table 6), among 16 sampling points surveyed, 2 sampling points have high Cd pollution ($160 \leq E_i < 320$), sampling point No. 2 (265.99) and sampling point No. 9 (190.82); 8 sampling points have higher Cd pollution ($80 \leq E_i < 160$); 5 sampling points have medium Cd pollution ($40 \leq E_i < 80$); and one sampling point have low Cd pollution ($E_i < 40$). Other four heavy metals Zn, Cu, Ni and Cr are at low pollution level ($E_i < 40$). From total potential ecological hazard risk index (RI), RI of all sampling points is in the range of $50 \leq RI < 300$ and belongs to the medium pollution level. Generally, change trend of heavy metal Cd in soil of different sampling points in different function areas is as follows: slag area > forest land > paddy field > non – irrigated farmland > orchard.

Secondly, relevant analysis indicates that in soil heavy metal content, only Ni and Cu are positively correlated. Since there is certain degree of Ni pollution in this deposit, the synergetic effect of Cu and Ni may deteriorate Ni pollution. In addition, from the perspective of the distance from sampling points to original ore processing shops, there is significantly negative correlation between heavy metal Cd, Zn and Cu and the distance, indicating that soil heavy metals fall with the increase in distance to the ore separation processing shop. Therefore, in agricultural and forestry production, to guarantee ecological security of foods, it is not appropriate to carry out production activities near the ore processing shops and slag stockpiling areas.

References

[1] Del RM, Font R, Almela C, et al. Heavy metals and arsenic uptake by wild vegetation in the Guadiamar river area after the toxic spill of the Aznalcollar mine[J]. Journal of Biotechnology, 2002, 98(1):125 – 137.

[2] Karathanasis AD, Johnson CM. Metal removal potential by three aquatic plants in an acid mine drainage wetland[J]. Mine Water and the Environmental, 2003, 22 (1) :22 – 30.

[3] DAI SG. Environmental chemistry (the 2nd edition)[M]. Beijing: Higher Education Press, 2006: 10. (in Chinese).

[4] Hossain MF. Khondaker M. Environmental contamination and seasonal variation on heavy metals in rice fields[J]. Research Journal of Chemistry and Environment, 2006, 10(1): 8 – 12.

[5] LIU DL. Mineral resources & development and utilization in Meizhou City [J]. Journal of Jiaying University, 2014,32(2):40 – 43. (in Chinese).

[6] LIU B. Study on the pollution of major mining areas in the upstream of Dahuofang Reservoir and evaluation on its potential ecological hazard[J]. Liaoning Urban and Rural Environmental Science & Technology, 2013, 33 (7): 56 – 58. (in Chinese).

[7] GB. Soil Environmental Quality Standards (GB 15618 – 1995)[S]. 1995 – 12 – 06. (in Chinese).

[8] LARS Hakanson. An ecological risk index for aquatic pollution control – Asedimentological approach[J]. Water Research, 1980(14):975 – 1001.

[9] CHENG F, CHENG JP, SANG HC, et al. Assessment and correlation analysis of heavy metals pollution in soil of Dajinshan Island[J]. Chinese Journal of Environmental Science, 2013,34(3):1062 – 1066. (in Chinese).

[10] XU ZQ, NI SJ, TUO XG, et al. Calculation of heavy metals' toxicity coefficient in the evaluation of potential ecological risk index[J]. Environmental Science and Technology, 2008, 31(2): 112 – 115. (in Chinese).

[11] ZHANG W, GE JT. Soil contamination by heavy metals and evaluations on potential ecological risks in an antimony mine[J]. Agricultural Science & Technology, 2015, 16(3):600 – 602.

(From page 53)

[16] Wuhan Education Bureau. Relying on community education, implementing the training of migrant workers' education[J]. Chinese Vocational and Technical Education,2006(9): 34 – 36. (in Chinese).

[17] GUO L. Community education: an effective way to promote migrant workers' urbanization – American Community Colleges' enlightenment to the continuing education of migrant workers[J]. Adult Education, 2013 (4): 124 – 126. (in Chinese).

[18] CHEN R. Study on the educational pattern of the new community in the process of the urbanization[D]. Fuzhou: Fujian Agriculture and Forestry University,2010. (in Chinese).

[19] CHEN JJ, CHEN LG. Study on the training and development of education of migrant workers[J]. Chinese Vocational and Technical Education,2011 (11): 30 – 35.. (in Chinese).

[20] DAI M, YUAN SS, LIU JJ. On the demand structure, supply mode and compensation mechanism of community services[J]. Journal of Jinan University,2011,33(4): 23 – 29. (in Chinese).

[21] LOU MQ. A study of the interactive development mechanism between local TV University and the migrant workers continuing education[D]. Shanghai: Shanghai Normal University,2011(2). (in Chinese).

[22] WANG SB, LAN L. Study on the main obstacles and route choice of the compensation education for new – age peasant workers under the background of industrial upgrading[J]. Journal of Anhui Agricultural Sciences, 2008,36(22): 9745 – 9747. (in Chinese).