ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 34 no. 4 pp. 93 - 100 2008

PL ISSN 0324-8461

ASSESSMENT OF SOIL HEAVY METALS POLLUTION IN DIFFERENT MINING ZONES OF A NONFERROUS METAL MINE

GUO LI LIAO

Mine Safety Technology Institute, China Academy of Safety Science & Technology
Beijing 100029, China

Keywords: Enrichment factors, geochemical baseline model, heavy metal, normalization procedure.

Abstract: The soil pollution features of heavy metals in a nonferrous metal mine were investigated. The contaminated soil area was divided into the tailing mineral, mineral drainage, settling dust with wind and mineral transportation zones. The concentrations of heavy metals in soil were detected by ICP-AES. A normalization procedure was established to construct the geochemical baseline model of soil environment. The pollution characteristics of heavy metals in soil were assessed by the baseline model. The seriously polluting metals are Zn (2805.2 $mg \cdot kg^{-1}$) and Pb (1709.2 $mg \cdot kg^{-1}$). Cd, Cu, and As only had pollution low-level in soil. Heavy metals pollution were mainly distributed in the mineral transportation zone, in which the average concentration of Zn, Pb, Cd, As, and Cu are 7958.5, 5808.3, 5.0, 66.7 and 344.4 $mg \cdot kg^{-1}$. The enrichment factors of Zn, Pb, Cd, Cu, and As were 986.8, 1303.8, 0.79, 0.89, and 4.31, respectively.

INTRODUCTION

The mining activities will pollute environment with heavy metals of various characteristics. The rapid development of industry and increasing release of agrochemicals into the environment has led to a growing public concern over the potential accumulation of heavy metals within soil. Recent rapid economic expansion in China means that heavy metal contamination of soils has become an increasingly serious problem [2, 8].

Heavy metals influence the environment with different type and strength depending on the concentration of organic matter and the physico-chemical factors such as pH value and ionic strength. Groundwater contamination and plant uptake may result in accumulation of heavy metals in the food chain, and then affect the living organisms. The risk of groundwater pollution depends on the retention, mobilization and transport of heavy metals in soils [5, 9].

The models of heavy metal transport play an important role in evaluating the potential risks [1, 6, 7, 15]. Therefore, the models are frequently used to describe and predict uptake and accumulation of heavy metals by plants or sorption and transport of heavy metals in soils and sediments. Calibration of models should be done using independent parameter with optimization programs instead of trial and error procedures to extract maximum information from the available data [11, 14, 17].

Herein, the contaminated soil area in a typical nonferrous metal mine was divided into four zones according to the pollution characteristics of heavy metals. And then, the normalization procedure was used to investigate the pollution features of heavy metals.

EXPERIMENTAL

Introduction of the mine

This mine was built in 1967 and yield 390 000 Mg lead-zinc mineral per year. Totally 9 042 000 Mg of mineral have been explored from 1967 to now. Nowadays, there are about 5 000 people living and working in the 50 km^2 mining area. The primary mineral metals are Pb and Zn associated with Cu, Ag, W, Sn, Mo, and Fe. The ore and rock contain 5–10% free SiO_2. The tailing dam covers an area of 1 km^2 which stores tailings of 5 000 000 m^3. The contaminated soil area was divided into four zones namely TPS (tailing mineral), MDPS (mineral drainage), DWPS (settling dust with wind), and MTPS (mineral transportation zone). In each zone, twenty-eight soil samples were randomly collected by triple sub-sampling technique. The pH value of soils was in a range of 5–9.7.

Reagents

All chemicals used were of analytical reagent grade. All solutions were prepared in deionized water (zero metal concentration). Calibration standards for each metal were prepared by appropriate dilution of stock solution of 1000 ppm of J.T. Baker/E. Merck standards.

ICP analysis

Concentrations of Zn, Pb, Cd, As, Sc and Cu were analyzed in all samples on a PS-6 ICP-MS (Baird, USA) according to the references [3, 4, 10]. A sample was put into the tetrafluoroethylene plastics crucible and 5 cm^3 HNO_3, 10 cm^3 HF, and 12 cm^3 $HClO_4$ was added. The sample was heated and the white smoke taken out. When the white smoke disappeard, the solution was chilled and 10 cm^3 HCl (1:1, v/v) was added. The solution was poured to a 50 cm^3 flask before determining. The analytical results are shown in Table 1.

NORMALIZATION ASSESSMENTS

Normalization method

The normalization method is commonly used in geochemical study. The inert elements in geochemical process are considered as standard in the normalization method. The correlationship between the inert elements and the activated element was evaluated by the enrichment condition of activated element. The correlation was also used to construct the linear regression equation, namely, baseline model [13, 20, 23]:

$$C_m = aC_N + b \tag{1}$$

where:

C_m stands for the concentration of heavy metal element,

C_N is the concentration of standard element,

a and b are the regression constants,

$\hat{C}_m$ is the anticipation value of C_m, which can be calculated by means of ascertaining regression constants; $\hat{C}_m$ is used as the baseline value of heavy metal elements.

Table 1. Concentrations of heavy metals

Zones	Serial number	Concentrations of heavy metals [mg·kg^{-1}]					
		Zn	Pb	Cd	As	Cu	Sc
TPS	1	2147.4	414.9	0.3	119.6	164.3	12.4
	2	3267	363.2	12.75	85.11	357.5	13.23
	3	2339	496.8	6.0	89.76	351.5	12.0
	4	8784	7932	19.5	1083.3	694	23.1
	5	5152	1625	19.50	207.4	417.9	16.5
	6	2704	224.8	2.75	86.63	344.2	12.86
	7	1521	568.4	5.25	108.9	369.6	7.1
	8	96.0	234.9	13.25	94. 4	339.4	3.56
	9	152.3	220.0	8.00	47.96	337.0	8.23
	10	888	81.6	0.5	80.47	327.3	10.2
MDPS	11	78.4	167.5	1.00	66.54	330.9	2.3
	12	59.7	46.9	0.6	42.5	410.1	5.6
	13	198.2	110.4	0.89	24	402.4	8.94
	14	215.6	104.5	2.3	18.9	345.6	10.21
	15	498.3	85.0	0.45	21.5	362.1	9.67
	16	1123	46.8	6.3	56.1	561.0	10.78
	17	768.1	71.5	7.5	71.5	318.9	9.8
	18	165	46.1	1.6	82.6	321.4	8.54
DWPS	19	234.1	48.2	4.6	114.1	322.1	9.6
	20	134.8	78.9	5.4	43.1	318.1	5.6
	21	214	16.8	1.60	39.8	343.5	7.89
	22	52.1	19.1	8.91	38.4	351.2	3.41
MTPS	23	9895.5	8234.1	7.01	59.3	341.0	24.3
	24	8976.2	9726.4	2.1	46.1	321	23.0
	25	9251	5893.8	4.12	167.1	351	23.9
	26	1100.9	1861.7	11.0	44.1	356.4	10.1
	27	9963.5	3241.2	0.7	37.2	377.9	24.6
	28	8564	5892.9	5.04	46.9	316.9	22.89

This geochemical method evaluates a ratio with an unlimited possible range instead of a certain concentration. An alternative approach to assess metal enrichment is the definition of normalized enrichment factors (EF):

$$EF = \left| \frac{(C_m / C_N)_{sample}}{(C_m / C_N)_{baseline}} \right| \tag{2}$$

Enrichment factors (EF) can fully reflect the influence of human being activities on the environment. By comparing the concentration of sample element with that of baseline element, the pollution degree was judged.

When EF was higher than 20, there existed serious contamination. When the enrichment factor was less than 1, there was no contamination. The polluted degree can be divided into six levels by means of EF (Table 2).

Table 2. Classification of enrichment factors

EF	Level	Pollution degree	EF	Level	Pollution degree
< 1	0	No	5–20	3	Intermediate-level
1–2	1	Minimal	20–40	4	High-level
2–5	2	Low-level	> 40	5	Intensity

Table 3. Baseline model and relative parameters

Baseline model	Relative Parameters	Prominence Level
Zn = -3.3892 + 0.5097Sc	0.9610	0.05
Pb = -2.7137 + 0.3639Sc	0.8509	0.05
Cd = 4.2249 + 0.1194Sc	0.151	0.05
As = -12.9838 + 9.9522Sc	0.3472	0.05
Cu = 329.303 + 2.7437Sc	0.2116	0.05

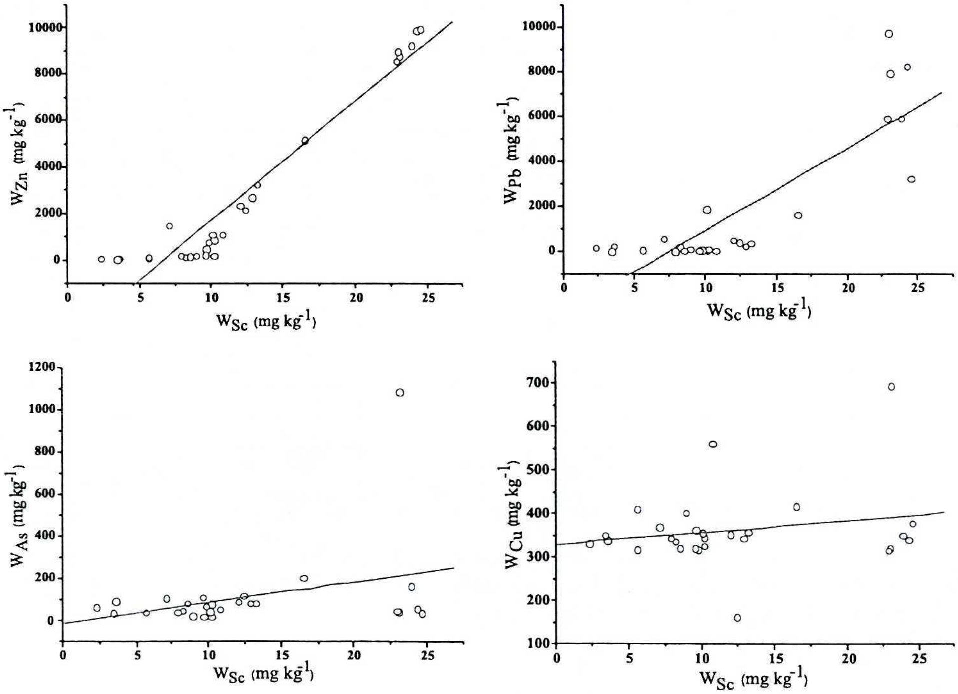

Fig. 1. Correlation and fit line between heavy metals and Sc

Construction baseline model

After the baseline model was constructed, the normalized element was selected. The selection of a normalized element depends on geological environment, human being implore situation, and environmental features. Aluminum is an important element in the aluminum silicate mineral and usually used to represent the standard of granularity change. Lithium is better than aluminum as normalization element for the crystal rock sediment.

When the heavy metals pollution is in low level, it is suitable to select Fe as normalization element [12, 16, 18, 21].

We wanted to ascertain the pollution features of heavy metals, so such heavy metals as Cr, Co, As, Hg, Pb, and Zn were eliminated. Herein, Sc was selected as normalization element. In China Sc was considered to be a normalization element in surveying the soil background value. Several survey results proved it unsuccessful [19, 22].

The baseline model and relative parameters between heavy metals and Sc required application of MATLAB computer software. The results are shown in Table 3 and Figure 1.

Assessment of contamination condition

Appling the acquired baseline model and equation (1), the enrichment factors and pollution levels are shown in Table 4.

Table 4. Enrich factor and class of contamination in soil near mine

Polluted kind	Serial number	Zn		Pb		Cd		As		Cu	
		EF	class	EF	class	EF	class	EF	class	EF	class
TPS	1	734	5	209	5	0.05	0	1.08	1	0.45	0
	2	966	5	183	5	2.2	2	0.71	0	0.98	0
	3	860	5	306	5	1.06	1	0.84	0	0.97	0
	4	1054	5	1421	5	2.87	2	4.97	2	1.77	1
	5	977	5	475	5	3.2	2	1.36	1	1.11	1
	6	837	5	113	5	0.49	0	0.75	0	0.96	0
	7	8947	5	315	5	1.05	1	1.86	1	1.06	1
	8	71	5	186	5	2.84	2	4.09	2	0.80	0
	9	223	5	763	5	1.54	1	0.7	0	0.96	0
	10	522	5	64	5	0.09	0	0.9	0	0.54	0
MDPS	11	35	4	89	5	0.22	0	6.65	3	0.99	0
	12	108	5	68	5	0.12	0	0.1	0	1.19	1
	13	166	5	203	5	0.17	0	0.32	0	1.14	1
	14	97	5	83	5	0.43	0	0.21	0	0.97	0
	15	292	5	107	5	0.08	0	0.27	0	1.02	1
	16	508	5	36	4	1.14	1	0.59	0	0.9	0
	17	451	5	85	5	1.39	1	0.84	0	0.89	0
	18	138	5	127	5	0.31	0	1.15	1	0.91	0
DWPS	19	137	5	63	5	0.86	0	1.37	1	0.91	0
	20	246	5	144	5	1.11	1	1.0	1	0.92	0
	21	354	5	88	5	0.31	0	0.61	0	0.98	0
	22	38	4	13	4	1.93	1	1.81	1	1.04	1
MTPS	23	1058	5	1386	5	0.99	0	5.36	3	0.87	0
	24	1077	5	1743	5	0.3	0	4.6	2	0.82	0
	25	1046	5	992	5	0.58	0	15.2	3	0.89	0
	26	647	5	2067	5	2.04	2	0.5	0	1.0	1
	27	1065	5	580	5	0.1	0	0.16	0	0.95	0
	28	1028	5	1055	5	0.72	0	0.22	0	0.81	0

The pollution levels of Pb and Zn are higher than 4, which demonstrated that Zn and Pb were the main contaminating elements. The pollution level of Cu in mining area was almost zero, which showed there was almost no Cu pollution. The pollution levels of Cd and As were in the range of 0–3, which showed there was little Cd and As pollution.

DISCUSSION

The enrichment factors in different polluted zones were compared (Figures 2–5).

In studying the class of heavy metals, it was determined according to calculated enrichment factor. Therefore the EF reflects the effect of human being on soil heavy metals. But the EF cannot reflect the soils pollution features and pollution association. So when we study the pollution features of soils heavy metals, we should either analyze the environmental geochemical and biology geochemical to study synthetically in order to acquire the full information on soil pollution.

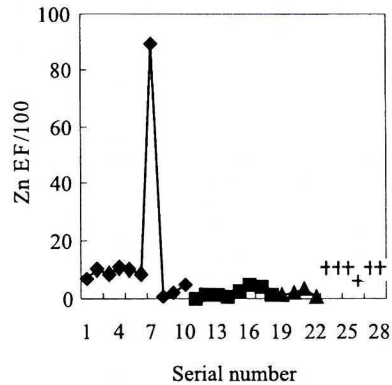

Fig. 2. The comparison of EF in different polluted zones of Zn
(◆– TPS, ▲ – DWPS, + – MTPS, ■ – MDPS, the same of Figs. 3–5)

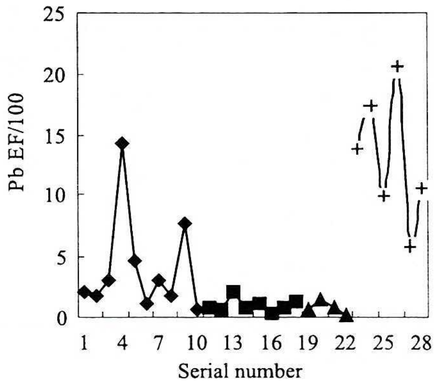

Fig. 3. The comparison of EF in different polluted zones of Pb

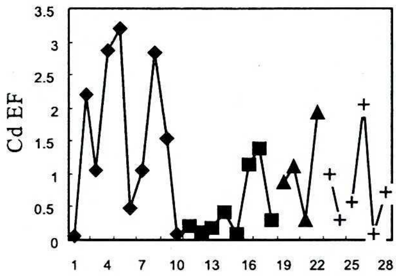

Fig. 4. The comparison of EF in different polluted zones of Cd

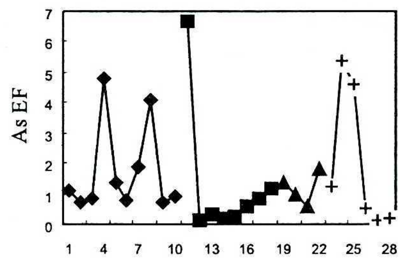

Fig. 5. The comparison of EF in different polluted zones of As

CONCLUSION

The pollution characteristics of heavy metals in soil were assessed by the baseline model. The seriously polluted metals are Zn and Pb. The pollution level of Cu in mining area was almost zero, which showed that there was almost no Cu pollution. The pollution levels of Cd and As were in range of 0–3, which showed little Cd and As pollution. The average concentration of Pb and Zn are 2805.1 mg·kg^{-1} and 1709.2 mg·kg^{-1}, respectively.

Acknowledgments

The authors are grateful for financial support from the Natural Science Foundation of China (50474050) and National Key Technology R&D Program (No. 2006BAK04B01-2).

REFERENCES

[1] Bleeker E.A.J., C.A.M. van Gestel: *Effects of spatial and temporal variation in metal availability on earthworms in floodplain soils of the river Dommel, The Netherlands*, Environmental Pollution, **148**, 824–832 (2007).

[2] Chen T.B., Y.M. Zheng, Z.C. Huang, H.T. Wu, H. Chen, K.K. Fan, K. Yu, X. Wu, Q.Z. Tian: *Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China*, Chemosphere, **60**, 542–551 (2005).

[3] Ettler V., M. Mihaljevic, O. Sebek, T. Grygar: *Assessment of single extractions for the determination of mobile forms of metals in highly polluted soils and sediments – Analytical and thermodynamic approaches*, Analytica Chimica Acta, **602**, 131–140 (2007).

[4] Garcia-Ruiz S., M. Moldovan, G. Fortunato, S. Wunderli, J.I.G. Alonso: *Evaluation of strontium isotope*

abundance ratios in combination with multi-elemental analysis as a possible tool to study the geographical origin of ciders, Analytica Chimica Acta, **590**, 55–66 (2007).
[5] Goyal P., P. Sharma, S. Srivastava, M.M. Srivastava: *Potential of Saraca indica leaf powder (SILP) for chromium removal from aqueous solution*, Archives of Environmental Protection, **33**(2), 35–44 (2007).
[6] Hobbelen P.H.F., J.E. Koolhaas, C.A.M. van Gestel: *Risk assessment of heavy metal pollution for detritivores in floodplain soils in the Biesbosch, the Netherlands, taking bioavailability into account*, Environmental Pollution, **129**, 409–419 (2004).
[7] Huang B., X. Shi, D. Yu, I. Öborn, K. Blombäck, H. Wang, W. Sun, F.L. Sinclair: *Environmental assessment of small-scale vegetable farming systems in peri-urban areas of the Yangtze River Delta Region, China*, Agriculture, Ecosystems and Environment, **112**, 391–402 (2006).
[8] Huang S.S., Q.L. Liao, M. Hua, X.M. Wu, K.S. Bi, C.Y. Yan, B. Chen, X.Y. Zhang: *Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China*, Chemosphere, **67**, 2148–2155 (2007).
[9] Konieczyński J., B. Komosiński, M. Żelechower: *Properties of particulate matter emitted from manufacturing of ceramic products*, Archives of Environmental Protection, **33**(2), 3–22 (2007).
[10] Kulkarni P., S. Chellam, D.W. Mittlefehldt: *Microwave-assisted extraction of rare earth elements from petroleum refining catalysts and ambient fine aerosols prior to inductively coupled plasma-mass spectrometry*, Analytica Chimica Acta, **581**, 247–259 (2007).
[11] Liu X., J. Wu, J. Xu: *Characterizing the risk assessment of heavy metals and sampling uncertainty analysis in paddy field by geostatistics and GIS*, Environmental Pollution, **141**, 257–264 (2006).
[12] Lu Y., Z.T. Gong, G.L. Zhang: *The Chemical Speciation of Heavy Metals of Urban Soil in Nan Jing*, Environ. Chem., **22**, 132–138 (2003).
[13] McGregor R.G., D.W. Blowes, J.L. Jambor: *The solid phase controls on the mobility of heavy metals at the Copper Cliff tailings arca Sudbury, Ontario Canada*, Contam. Hydrol. **33**, 247–271 (1998)
[14] Michel K., B. Ludwig: *Modelling of seepage water composition from experiments with an acid soil and a calcareous sediment*, Acta Hydrochimicaet Hydrobiologica, 33, 595–604 (2005).
[15] Michel K., M. Roose, B. Ludwig: *Comparison of different approaches for modelling heavy metal transport in acidic soils*, Geoderma, **140**, 207–214 (2007).
[16] Michelle P.B., C.L. Adrienne: *A comparative mineralogy of the vadose zone of sulfide mine tailings at two sites in New Mexico USA*, Environ. Geol., **33**, 130–142 (1998).
[17] Mil-Homens M., R.L. Stevens, I. Cato, F. Abrantes: *Regional geochemical baselines for Portuguese shelf sediments*, Environmental Pollution, **148**, 418–427 (2007).
[18] Sun H., B. Sun, T.L. Zhang: *Assessment of Pollution of Heavy Metal on Vegetable Field Around Guixi Smetltery, Jianxi Province*, J. Agro-Environ. Sci., **22**, 70–72 (2003).
[19] Teng Y.G., C.Y. Huang, J. Long: *Studies on soil enzymatic activities in areas contaminated by tailings from Pb, Zn, Ag mine*, China Environmental Science, **22**, 551–555 (2002).
[20] Teng Y.G., S.J. Ni, X.G. Tuo: *Application of a Normalization Procedure in Assessing Heavy metal Pollution*, Acta Pedological Sinica, **40**, 374–379 (2003).
[21] Wang Q.R., X.M. Liu, Y.S. Cui: *Soil Contamination and Heavy Metals at Individual Sites of Industry and Mining Associate with Wastewater Irrigation in China*, Acta Sciential Circumstiae, **22**, 354–359 (2002)
[22] Wei G.J.: *Mining environmental engineer [M], Beijing*, Metallurgy industries publish company, 2001.
[23] Zhang C.L., H.Y. Bai: *Application fuzzy mathematics assessment on soil heavy metals pollution*, Guan Xi Science of Agriculture Biology, **22**, 54–57 (2003).

Received: August 23, 2007; accepted: June 25, 2008.