

Evaluation of Heavy Metals Around the Mining of Decorative Stone Ore in Susong County Liaohe River

SiHeng Lu, Chang Pan, YuJuan Jin, Xiang Wang, Xinlai Wei, ZhiMin Yu

Department of Biology and Environment Engineering, Hefei University, Hefei 230601, P. R. China.

Address: No. 99, Jinxiu Road, Hefei 230601, P. R. China. * Corresponding author. e-mail: 1035319332@qq.com

Abstract. In order to study the pollution of heavy metals around Liaohe Fender stone mine in Susong County, the soils at six points and the sediment at four points were selected. The effects of heavy metals Cu, Zn, Pb, Cd, Cr, Ni, Hg and As were measured, the single factor index and the Nemero index method were used to evaluate the heavy metal elements in soil and sediment. The results showed that the values of heavy metal elements in the soil and sediment were less than 1 and the $P_{integrated}$ values were less than 0.85, the mine area was not polluted by heavy metals and belonged to the clean area within the grade I.

Keywords:- ore rock, heavy metal; soil sediment, the single factor index, the nemero index.

I RESEARCH AREA

In this paper, the mining area is the open pit mining and main mining marble, the amount of ore 110.7729 million m³, the range of 1.4064 square kilometers. The mining area is located in the north of Susong County, and the geographical coordinates of the center of the mining area are E 115 ° 55'25 " and N 30 ° 21'37". The mining area is 71 km from the Changjiang Fuxing Town Pier, by the revival of the town pier along the Yangtze River golden waterway east to Shanghai.

II THE PURPOSE AND SIGNIFICANCE OF THE STUDY

Long-term mining of the mine not only caused soil erosion, but also led to the long-term enrichment of heavy metals during the mining process, and caused a serious threat to the surrounding soil environment.

Heavy metal generally refer to metals with a density greater than or equal to 5.0 [1], which is non-degradable persistent toxic pollutants, that dissolve, adsorb, precipitate, complex and so on in a series of migration and enrichment process in the soil [2], not only caused serious harm to the soil environment and water environment, But also through the food chain

into the human body and accumulated, leading to health problems. In this paper, multi-method has been used to evaluate the heavy metal elements in the mining area, it is of great significance to provide the basis for the content of heavy metals in the mining area and to better manage the mining environment.

III EXPERIMENT AND DATA PROCESSING

A. Sample collection

In the sampling area using a checkerboard sampling points, collecting the thickness of the soil in the 0-20cm deep 6 points of the soil, where each point of soil samples were equely mixed with quartiles [3], the collected samples into the polyethylene plastic bag, and take back to the laboratory. The collection of its sediment along the river to the direction, a sample of 4 points was collected from the sediment layer using a sediment sampler, each sample was taken at a rate of 10 cm for one time [4], then mixed into a sealed bag and numbered back to the laboratory. The sampling points for soil and sediment are shown in Table 2.1 and Table 2.2 below:

Table 2.1
Soil Point Arrangement

Point number	Sampling point	Location	Detection Indicator
S1	Farmland on the south side of the mining area 20cm	N : 30°19'29" E : 115°57'26"	pH, Cd, Hg, As , Cu, Pb, Cr, Zn , Ni
S2	Farmland on the south side of the mining area 50cm		
S3	Farmland on the south side of the mining area 100cm		
S4	Forest on the north side of the mining area 20cm	N : 30°19'29" E : 115°57'16"	
S5	Forest on the north side of the mining area 50cm		
S6	Forest on the north side of the mining area 100cm		

Table 2.2
Placement of The Sediment

Point number	Sampling point	Detection Indicator
1#	Changxi River downstream of the sewage outfall 5000m	pH, Cd, Hg, As, Cu , Pb, Cr, Zn, Ni
2#	Changxi River downstream of the sewage outfall 2000m	
3#	Changxi River downstream of the sewage outfall 500m	
4#	Changxi River sewage outfall upstream 500m	

B. Pretreatment of the sample

Take 500g of soil samples and sediment on the tray in the natural air-dried, polished in the glass, filter with 100 mesh nylon screen [5].

(1) Method for digestion of Cu - Zn - Cd - Cr Ni heavy metal hydrochloric acid - nitric acid - hydrofluoric acid - perchloric acid [6].

Weigh the soil and sediment (0.2 ~ 0.5g) into the digestion cup, wet with water and add 10 mL of hydrochloric acid to heat up to 3 mL on a hot plate at 80 ° C, the addition of nitric acid and hydrofluoric acid 5mL and 3mL of high chloric acid, then heated until the contents of the digestion cup were viscous, and the digestion cup was washed with deionized water and transfer the contents to a 50 mL volumetric flask.

(2) Determination of As Sulfuric Acid - Nitric Acid - Perchloric Acid [7].

Weigh 0.20 ~ 0.5g sieve and sample into the 150mL Erlenmeyer flask, add 7mL sulfuric acid,

10mL nitric acid and 2mL perchloric acid, heating on the hot plate until the liquid was white residue, adding distilled water to 50mL.

(3) Digestion of Hg sulfuric acid - nitric acid - potassium permanganate [8].

Weigh 0.2 ~ 0.5g sieve soil samples and sediment into 150mL Erlenmeyer flask, add sulfuric acid, nitric acid mixture 5 ~ 1mL and 10mL potassium permanganate, in the hot plate for 30 ~ 60min. Remove the cooling, add hydroxylamine hydrochloride solution until brown, add distilled water to 100mL.

C. Standard curve preparation

According to the approximate range of the detection limit of each heavy metal Cu1mg / Kg, Zn0.5mg / Kg, Pb and Cd 0.2mg / Kg, Cr and Ni0.5mg / Kg [9], preparation of the standard curve, the final transfer to 50mL capacity bottle, the marking gradient is shown in Table 2.3:

Table 2.3
Concentration Gradient of Each Element

Mixed standard volume /mL	0.00	0.50	1.00	2.00	3.00	5.00
Cu (mg/L)	0.00	0.20	0.40	0.80	1.20	2.00
Zn (mg/L)	0.00	0.10	0.20	0.40	0.60	1.00
Pb (mg/L)	0.00	0.50	1.00	2.00	3.00	5.00
Cd (mg/L)	0.00	0.025	0.005	0.10	0.15	0.25
Cr (mg/L)	0.00	0.50	1.00	2.00	3.00	4.00
Ni (mg/L)	0.00	0.20	0.50	1.00	2.00	3.00
Hg (mg/L)	0.00	0.50	1.00	2.00	3.00	4.00
As (mg/L)	0.00	0.50	1.00	1.50	2.00	3.00

D. Sample test results

(1) Instrument type and related parameters

The Cu,Zn,Cd,Cr and Ni heavy metals were characterized by flame atomic absorption spectrophotometry(Model AA900),for Hg cold atomic using absorption spectrometer (F732-VJ), As

using UV-Vis spectrophotometer (Uvmini1240), The parameters of the relevant elements of flame atomic absorption are shown in Table 2.4 [10], The determination method and the minimum detection limit for each heavy metal are shown in Table 2.5:

Table 2.4
Parameters of Flame Atomic Absorption Related Elements

copper parameter	Wavelength (nm)	Slit width(nm)	Lamp current(mA)	Acetylene: air
Cu	324.8	0.8	2.0	1:5-1:6
Zn	213.9	0.2	2.0	1:4
Pb	283.3	0.8	2.0	1:4
Cd	228.8	0.8	2.0	1:5-1:6
Cr	357.9	0.2	4.0	1:2-1:3
Ni	232.0	0.2	3.0	1:4

Table 2.5
Determination of Heavy Metals and Minimum Detection Limit

Detection Indicator	Detection method	testing base	Detection limit or minimum detection concentration
pH	Potential method	NY/T 1377-2007	--
Cd	KI-MIBK Extraction Flame Atomic Absorption Spectrophotometry	GB/T 17140-1997	0.05
Hg	Cold atomic absorption spectrophotometry	GB/T 17136-1997	0.005
As	Silver dimethyldithiocarbamate spectrophotometric method	GB/T 17134-1997	0.5
Cu	Flame Atomic Absorption Spectrophotometry	GB/T 17138-1997	1.0
Pb	KI-MIBK Extraction Flame Atomic Absorption Spectrophotometry	GB/T 17140-1997	0.2
Cr	Flame Atomic Absorption Spectrophotometry	HJ 491-2009	5
Zn	Flame Atomic Absorption Spectrophotometry	GB/T 17138-1997	0.5
Ni	Flame Atomic Absorption Spectrophotometry	GB/T 17139-1997	5

(2) Heavy metal elements Soil and sediment measurements Data Table 2.6 and Table 2.7:

Table 2.6
Soil Element Measurement Data

Detection Indicator	S1	S2	S3	S4	S5	S6	unit
pH	6.87	7.21	7.38	7.46	7.04	7.33	Dimensionless
Cd	0.021	0.020	0.032	0.07	0.07	0.07	mg/kg
Hg	0.012	0.015	0.017	0.008	0.011	0.012	mg/kg
As	4.35	5.15	4.58	8.51	6.31	5.89	mg/kg
Cu	16.1	12.3	15.0	15.1	10.3	10.2	mg/kg
Pb	4.18	4.10	4.57	15.6	15.5	12.0	mg/kg
Cr	32.8	32.9	31.9	44.3	42.5	37.2	mg/kg
Zn	1.52	1.59	1.46	5.95	5.63	6.03	mg/kg
Ni	12.7	14.8	12.3	36.1	30.7	18.3	mg/kg

Table 2.7
Sediment Element Measurement Data

Detection Indicator	1#	2#	3#	4#	unit
pH	7.34	7.81	7.22	7.63	Dimensionless
Cd	0.035	0.022	0.029	0.035	mg/kg
Hg	0.012	0.009	0.010	0.015	mg/kg
As	0.32	0.26	0.28	0.19	mg/kg
Cu	5.1	0.8	1.36	9.96	mg/kg
Pb	4.18	0.16	2.01	9.93	mg/kg
Cr	25.3	4.2	4.6	27.9	mg/kg
Zn	7.47	0.23	0.10	28.1	mg/kg
Ni	13.2	2.3	3.4	11.6	mg/kg

IV EVALUATION AND ANALYSIS OF RESULTS

Evaluation of soil environmental quality is generally based on the standard limits of «Soil Environmental Quality Standard» (GB15618-1995) [11]. In this paper, we mainly use the single factor and Nemer index to evaluate the content of various metal elements in the soil.

A. Soil pH grade and soil metal element background values

For the pH in the soil, the soil scientist uses it to represent the hydrogen ion concentration in the soil sample [12]. We usually use the pH value to represent the relative pH, through the determination of pH, you can generally understand the evaluation of soil quality in the region, but also for the background of the various elements of the soil to provide a corresponding reference basis [13], The soil pH grades are as follows: Table 3.1:

Table 3.1
Classification of Soil pH

pH	<4.5	4.5~5.5	5.5~6.0	6.0~6.5	6.5~7.0	7.0~7.5	7.5~8.5	8.5~9.5	>9.5
rank	Very strong acidity	Strong acidity	acidity	Weak acidity	neutral	Weakly alkaline	alkaline	Strong alkaline	Very strong alkaline

Soil background value refers to the composition and content of chemical elements in the soil which are not affected by human activities [14]. Soil background value is not only the standard of

environmental quality, but also the basis of various soil pollution evaluation methods [15]. The soil environmental quality standards (GB15618-1955) mg / kg as shown in Table 3.2:

Table 3.2
 Soil Environmental Quality Standard (GB15618-1955)

Soil pH	Level one		Level two		Levelthree	
	Natural background	<6.5	6.5~7.5	>7.5	>7.5	
Cd≤	0.2	0.3	0.3	0.6	1.0	
Hg≤	0.15	0.3	0.5	1.0	1.5	
As	Paddy fields≤	15	30	25	20	30
	dry land≤	15	40	30	25	40
Cu	Farmland n≤	35	50	30	100	400
	orchard≤	--	150	100	100	400
Cr	Pb≤	35	250	300	350	500
	Paddy fields≤	90	250	300	350	400
	dry land≤	90	150	200	250	300
	Zn≤	100	200	250	300	500
Ni≤	40	40	50	60	200	

B. Single Factor Index and Nemer Index

The so-called single factor evaluation is the evaluation of the degree of influence on an element or compound in the soil [16]. The evaluation is based on the individual accumulation index P_i of the material. The advantage of this method is that these transformations are linear, and the value of the attribute before and after the change is proportional [17], only need to calculate the individual indicators of soil elements and the calculation is relatively simple [18]. The single factor pollution index

environmental quality evaluation criteria in Table 3.3 [19]:

Single factor index formula [20]:

$$P_i = \frac{C_i}{S_i} \quad (1)$$

Where P_i - soil i pollutant environmental index;
 C_i - Measured concentration of soil i contaminants (mg / kg);
 S_i - soil i pollutants evaluation criteria (mg / kg) (generally take II types of standards);

Table 3.3
 Single Factor Pollution Index Environmental Quality Evaluation Standards in Table

rank	P_i value	Comparison of measured and background values	Pollution assessment
I	$P_i \leq 1$	similar	No pollution
II	$1 < P_i \leq 2$	Higher than the background value below the pollution start value	Slight contamination
III	$2 < P_i \leq 3$	Higher than the pollution start value	Mild contamination
IV	$3 < P_i \leq 5$	More than 1 times the initial value of pollution	Moderately polluted
V	$P_i > 5$	More than 2 times the initial value of pollution	Severe pollution

The comprehensive evaluation method for a region can be used to evaluate the multi - factor, including the Nemeru comprehensive index method and the overlap index method with weights. In this paper, the evaluation of the heavy metal elements in the soil is mainly based on the Nemeru comprehensive index method. The advantage is not only to consider the average accumulation of various chemical elements of the material level, but also reflects the accumulation of the most serious chemical substances to the extent of the harm to the environment [21]. The evaluation criteria for the

environmental quality of the Nemeru pollen index are shown in Table 3.4 [22]:

Nemeru comprehensive index method formula [23]:

$$P_{integrated} = \sqrt{\frac{(C_i / S_i)_{max}^2 + (C_i / S_i)_{av}^2}{2}} \quad (2)$$

Where $P_{integrated}$ - a comprehensive pollution index in a region;
 $(C_i / S_i)_{max}$ - the maximum pollution index in soil contaminants;
 $(C_i / S_i)_{av}$ - the average pollution index in soil contaminants;

Table 3.4
Nemero Pollutants Environmental Quality Assessment Criteria

rank	Pintegrated value	Comparison of measured and background values	Pollution assessment
I	Pintegrated ≤ 0.85	A variety of metals are at the background level	Clean (safe)
II	$0.85 < \text{Pintegrated} \leq 1.75$	One or more of the background values	Mild contamination
III	$1.75 < \text{Pintegrated} \leq 2.56$	One or more of which has clearly exceeded the background value	Moderately polluted
IV	Pintegrated > 2.56	One or more has far exceeded the background value	Severe pollution

C. Soil and Sediment Single Factor Index and Nemerot Pollution Index

According to the range of pH, to determine the environmental quality standard selected soil background value of the evaluation level, and then through the single factor index and Nemerot pollution

index evaluation formula calculated data, the Nemerot pollution index are shown in Table 3.5, single factor sediment soil data are shown in Table 3.6, Integrated Pollutant Soil Index are shown in Table 3.7 and Integrated Pollution Index Sediment Index are shown in Table 3.8.

Table 3.5
Single Factor Soil Data

Detection Indicator	S1	S2	S3	S4	S5	S6
Cd	0.070	0.067	0.107	0.233	0.233	0.233
Hg	0.024	0.030	0.034	0.016	0.022	0.024
As	0.145	0.172	0.153	0.284	0.210	0.196
Cu	0.537	0.410	0.500	0.503	0.343	0.340
Pb	0.014	0.014	0.015	0.052	0.052	0.040
Cr	0.164	0.165	0.160	0.222	0.213	0.186
Zn	0.006	0.006	0.006	0.024	0.023	0.024
Ni	0.254	0.296	0.246	0.722	0.614	0.366

Table 3.6
Single Factor Sediment Data

Detection Indicator	1#	2#	3#	4#
Cd	0.117	0.073	0.097	0.117
Hg	0.024	0.018	0.020	0.030
As	0.013	0.010	0.011	0.008
Cu	0.170	0.027	0.045	0.332
Pb	0.014	0.001	0.007	0.033
Cr	0.084	0.014	0.015	0.093
Zn	0.030	0.001	0.000	0.112
Ni	0.264	0.046	0.068	0.232

Table 3.7
Integrated Pollutant Soil Index

Point	S1	S2	S3	S4	S5	S6
Pintegrated value	0.395	0.308	0.370	0.542	0.459	0.286

Table 3.8
 Integrated Pollution Index Sediment Index

point	1#	2#	3#	4#
Pintegrated value	0.197	0.055	0.071	0.243

In order to visually and clearly compare the pollution of each point, The Pintegrated value of the each soil and sediment points are shown in a histogram shown in Figure 3.1 and 3.2:

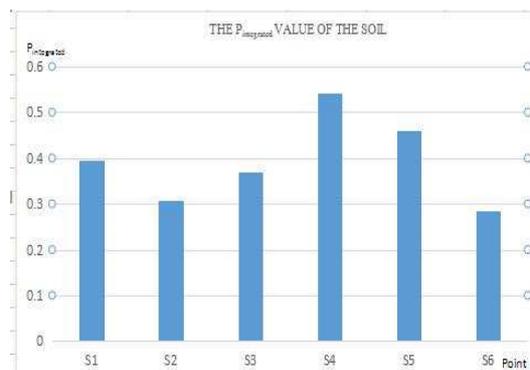


Figure 3.1 Soil Pintegrated Value

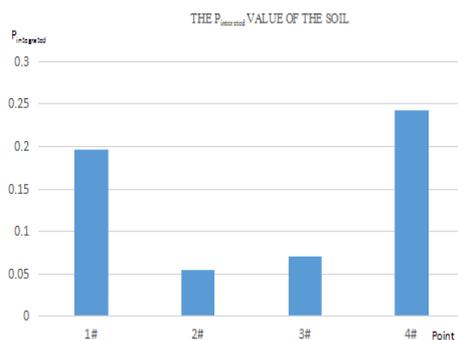


Figure 3.2 Sediment Pintegrated Value

D. Results analysis and summary

The results of the evaluation of soil and sediment according to single factor index and Nemerot pollution index method are as follows:

single factor index evaluation

The results of six points and four sediment points calculation of soil using single factor index formula show that show that the Pi value of Cu in soil 1 ~ 4 is the highest and the pollution of Cu is the most serious. Point Pi and S6 Ni Pi value of the largest, Ni pollution is most serious. The Pi values of S1, S2, S3 and S6 Zn are the smallest and the pollution of Zn is the smallest. The Pi value of 1 # and 4 # Ni in the sediment is the highest, the Ni pollution is the most serious, the Pi value of 2 # and 3 # Cd is the largest, the Cd pollution is the most serious, the Pi value of 1 # As is the smallest, the As pollution is the lightest, and Pi value of 3 # Zn is the smallest, Zn pollution is the lightest, the Pi value of 4 # Hg is the smallest, and the pollution of Hg is the lightest.

The results of single factor index show that the Pi values of soil and sediment are less than 1, belong to

grade I, and there is no heavy metal pollution compared with soil environmental quality standard (GB15618-1955).

(2) The Calculation Results of Soil and Sediment at the Point of Nemerot Pollutant Index

The results show that the Pintegrated value of S4 is the largest and the pollution is the most serious, and the Pintegrated value of S6 is the smallest and the pollution is the lightest. Sediment 4 #Pintegrated maximum value of the most serious pollution,3 # Pintegrated minimum value of the smallest, the smallest pollution.

The calculation of the pollution index from Nemerot indicated that the Pintegrated value of soil and sediment was less than 0.85 and belonged to grade I, and there was no pollution compared with soil environmental quality standard (GB15618-1955).

The results of the evaluation of soil and sediment by single factor index and Nemerot pollen index show that the contents of Cu, Ni and Cd in heavy metals around Liaohé facade stone mining are relatively high. Zn, Hg content is relatively low, but according to the soil environmental quality standards (GB15618-1955) to evaluate, are within the level of I, and no heavy metal pollution. From the two evaluation criteria of the mining area of heavy metal control is better, the environment did not bring a greater threat.

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