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The Heavy Metal Pollution Characteristic and Ecological Risk Assessment of a Lead and Zinc Smelting Slag Waste Land in North China

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Abstract **-**In North China, an abandoned land of previous lead and zinc smelting slag pile was investigated by random points method. A total of 16 surface soil samples in two contaminated sites was collected by using the method of random points method. While 8 surface soil samples was collected by random sampling in an uncontaminated site nearby as control. The total content of six major heavy metals (As, Cd, Cr, Cu, Pb, Zn) was analyzed. The methods of Single Pollution Index (SPI), Nemerow Pollution Index (NPI), Hakanson Potential Ecological Index (HPEI) were applied to assess the ecological risk of the contaminated site. The result shows that the content of Cd control site(#1) was almost 25 times greater than background value, the mean content of Pb and Cd in surface soil at contaminated sie (#2) respectively are 318.23 and 1448.3 times as high as the local soil element back ground value, the mean content of Pb, Zn, Cd in the surface soil at contaminated site (#3) are 1141.98, 591.11 and 1165.53 times as high as the local soil element back ground value. This research shows that the soil environment quality of pollution area and around were affected significantly by industrial activity. The Nemerow Pollution Index of soil heavy metal at three site（#1，#2，#3）are 2.13，15.61 and 70.09 respectively, while the assessment result are 7.2，245.1 and 393.5 for the three site by Hakanson Potential Ecological Index method, which rank respectively of slight, medium and extremely strong ecological risk rating. According the evaluation result, the study area exist certain ecological risk, which is needed to take appropriate risk control measures, in order to prevent further soil pollution and ensure the healthy rights and interests of factory workers.

Keywords**:** lead and zinc smelting abandoned wasteland; heavy metal; risk assessment

1. Introduction

Rapid rise and booming township enterprises are the main driving force of rapid economic growth in rural China since its reform and opening up, but outdated equipment and backward technologies cause seriously damage to the local environment and resources (Shan and Wang, 2009), especially made for lots of soil pollution. Soil is one of the most basic natural resources to the survival of humans, but the industries in the villages and towns such as electroplating, metallurgy, chemical engineering, oil refining, textile printing, oil vanish, leather and so on, have brought farmland contaminated and made lots of industries and mining waste site in rural China. The main pollutant of village and towns are excessive amounts of poisonous and harmful heavy metals. Heavy metals are non-biogradable and have a certain mobility and bioavailability, and even further effect human health through the food chain.(Sun et al., 2007; Wu et al., 2007). Therefore, it is become an important issue in China to strengthen preventing rural industries pollution and to improve rural soil ecological environment.

There are many small township enterprises involving electroplating, metallurgy, chemical engineering industries, which have not only caused serious soil contaminated and potential ecological risk, and are very close to residential area and farmland. In this study, a variety of evaluation methods are used to assess the ecological risk of a slag heap abandoned land at a metal smelting factory in Baoding city (Xie and Wang, 2002).

2. Materials and Methods

2. 1. General Situation of the Polluted Sites

The study site is located in an abandoned factory in the eastern part of Qingyuan District, Baoding, Hebei province, China, where small non-ferrous metallurgy enterprises are densely distributed. The investageted site has three parts which can be divided as site #1, site #2 and site #3(Fig. 1). A pollution-free at site #1 was used as a reference field. Site #2, which has been abandoned for almost 20 years, is contaminated by slaggy from the pyrometallurgy of lead, while site #3, abandoned for 8 years, is polluted by the waste residue of zinc hydrometallurgy (Liu et al., 2011).

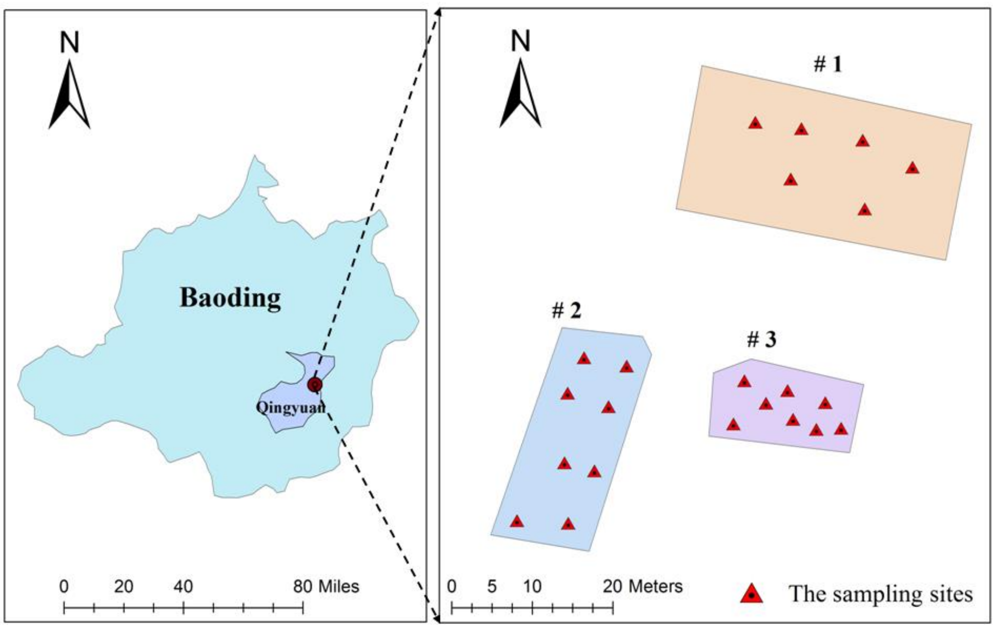

Fig. 1. Sampling Site in a township metallurgy factory of North China(Qingyuan District, Baoding)

2. 2. Sample Collection and Analysis

Six surface (0-20 cm) samples are collected by using a random point method at site #1, eight surface samples at site #2 and site #3. Soil samples were air-dried, ground and passed through a 100 mesh plastic sieve and then digested and the total metal concentrations (As, Cd, Cr, Cu, Pb, Zn,) in digestates were then determined by ICP-AES(Liu et al., 2014).

2. 3. Evaluation Methods of Site Contamination

Single Pollution Index (SPI) and Nemerow Pollution Index (NPI) are used to assess the degree of contamination, references to the quality criteria of soil environment (GB 15618-1995) and the Standard of Soil Quality Assessment for Exhibition Sites (HJ 350-2007). The classification of environment quality of the soil by NPI method is shown in Table. 1.

Table. 1. Classification of environment quality of the soil by NPI.

PI	First Class	Second class	Third class	Fourth class	Fifth class
	Clean(Safe)	Fairly clean (warning line)	Slightly polluted	Moderately polluted	Serious polluted
P_i	$P_i \leqslant 0.7$	$0.7 < P_i \leqslant 1.0$	$1.0 < P_i \leqslant 2.0$	$2.0 < P_i \leqslant 3.0$	$P_i > 3.0$

Hakanson Potential Ecological Index is applied to assess the ecological risk of the contaminated sites, which is calculated as following formulas: (Xu, et al., 2014; Du et al., 2015; Wu et al., 2015)

The potential ecological risk factor which represents the ecological risk of one heavy metal element is calculated as follows:

$$E^i_r = T^i_r \times C^i_f = T^i_r \times C^i_{\mathrm{surface}}/C^i_{\mathrm{n}} \tag{1}$$

The potential ecological risk index (RI) which represents the ecological risk of various heavy metal element is calculated as follows:

$$RI = \sum_{i=1}^{\mathrm{n}} E^i_r \tag{2}$$

The meanings of the parameters in the formulas above are as follows:

T^i_r: the toxic response factor of each heavy metal element, which reflects heavy metals in the water phase, sedimentary response of the relationship between solid phase and the biological phase.

C^i_f: contamination factor of one heavy metal element;

C^i_{surface}: The measured value of soil (or sediment) contamination concentration;

C^i_n: reference value in calculating.

Hakanson pointed out the highest background value of sediments before morden industrialization can be used as reference value, some scholars used the national soil environment standard as reference value. This research uses the standardized T^i_r made by Hakanson as evaluation basis, which are Cr=2, Zn=1, Cu=5, As=10, Cd=30, Pb=5(Hakanson, 1980). According to the requirement of remediation, Standard of Soil Quality Assessment for Exhibition Sites (Grade B) is used as benchmark. Grading standard of potential ecological risk of heavy metal pollution is shown in Table. 2.

Table. 2. Indices and grades of potential ecological risk of heavy metal pollution.

Potential ecological risk factor E^i_r	Potential ecological risk index RI	Contamination degree
$E^i_r < 40$	$RI < 150$	slight
$40 \leqslant E^i_r < 80$	$150 \leqslant RI < 300$	medium
$80 \leqslant E^i_r < 160$	$300 \leqslant RI < 600$	strong
$160 \leqslant E^i_r < 320$	$RI \geqslant 600$	very strong
$E^i_r \geqslant 320$		extremely strong

2. 4. Data Analysis

Statistics and data analysis are calculated by Microsoft Excel 2007 and SPSS 18.0, AutoCAD 2011 is used for graphics.

3. Soil Heavy Metal Content Analysis

3. 1. Soil Heavy Metal Content Analysis

Six heavy metals concentration of three sites were shown in Table 3. Table 3 shows the average content of site #1 about six heavy metal elements (As, Cd, Cr, Cu, Pb, Zn) are 15.79, 1.86, 48.18, 28.96, 110.41, 442.88 mg/kg. The mean concentrations are higher than the background value of Hebei province and the whole Nation except the element Cr and Cu. The mean concentrations of As, Cd, Pb, Zn are 1.81，24.85，5.52 and 5.65 times than the background value of Hebei province. The coefficient of variation of six heavy metals show that while site #1 has no obviously contamination, but the coefficient of variation of Zn and Pb are higher than usual. This result suggests that the abnormally high concentration of Zn and Pb at site #1 are greatly influenced by the melting activities nearby and the heavy metal pollutants may be from the sedimentation of heavy metals in atmosphere and surface runoff. Site #2 is a slag heap made by pyrometallurgy of lead. The mean pH value is 7.35 in site #2, which has a mean concentration of 276.85 ,108.63, 57.83, 385.35, 6364.58, 6949.34 mg/kg for As, Cd, Cr, Cu, Pb, Zn respectively. This result shows the concentration of five heavy metals (As, Cd, Cu, Pb, Zn) are seriously exceeding the local and national background value, which are 31.82, 1448.40, 7.20, 318.23, 88.64 times than soil backround value of Hebei province. The variance coefficient of As Cd, Cu, Pb are higher, which the abnormally high concentration of the four heavy metals are related to man-made pollution. Site #3 is a slag heap waste site made by zinc hydrometallurgy process, which is slightly acidic with the mean pH value of 6.35. The mean content of As, Cd, Cr, Cu, Pb, Zn are 372.37, 87.42, 116.28, 439.65, 22839.68, 46343.24 mg/kg respectively. Except Cr, the content of other five heavy metals far surpasses the local soil background value , especially the concentration of Pb and Zn exceed 2×10^4mg/kg . The coefficient of variation of As, Cd, Cu, Zn are higher. It suggests that human activity have a significant impact on them (Wang et al., 2009; Yao et al., 2014).

Table. 3. Characteristics of heavy metal concentrations in soils of three site (mg/kg).

		As	Cd	Cr	Cu	Pb	Zn
Background value	National	11.20	0.097	61.00	22.60	26.00	74.20
	Lcoal (Hebei)	8.70	0.075	63.90	53.50	20.00	78.40
#1	Max	27.00	2.54	57.33	35.93	184.66	616.61
	Min	9.40	0.23	31.31	21.09	39.92	179.04
	Medium	14.24	2.20	51.88	29.31	122.19	512.35
	AVG	15.79	1.86	48.18	28.96	110.41	442.88
	CV(%)	38.00	46.00	21.00	18.00	46.00	38.00
	K_1	1.81	24.85	0.75	0.54	5.52	5.65
#2	Max	791.95	621.10	72.09	1402.10	18220.30	11461.40
	Min	71.59	7.80	36.18	96.29	1961.88	1749.88
	Medium	141.89	11.89	58.05	239.79	4603.37	7550.24
	AVG	276.85	108.63	57.83	385.35	6364.58	6949.34
	CV(%)	95.00	196.00	21.00	110.00	87.00	66.00
	K_1	31.82	1448.40	0.91	7.20	318.23	88.64
#3	Max	847.67	164.17	162.93	955.50	28514.30	71560.30
	Min	125.75	23.81	65.66	106.76	6070.70	16246.70
	Medium	329.63	80.02	118.15	412.53	26058.60	47760.45
	AVG	372.37	87.42	116.28	439.65	22839.68	46343.24
	CV(%)	63.00	57.00	25.00	55.00	33.00	40.00
	K_1	42.80	1165.53	1.82	8.22	1141.98	59111.00

Annotation：$K_1=C_{surface}/C_{local}$

3. 2. Assessment of Soil Heavy Metal Pollution

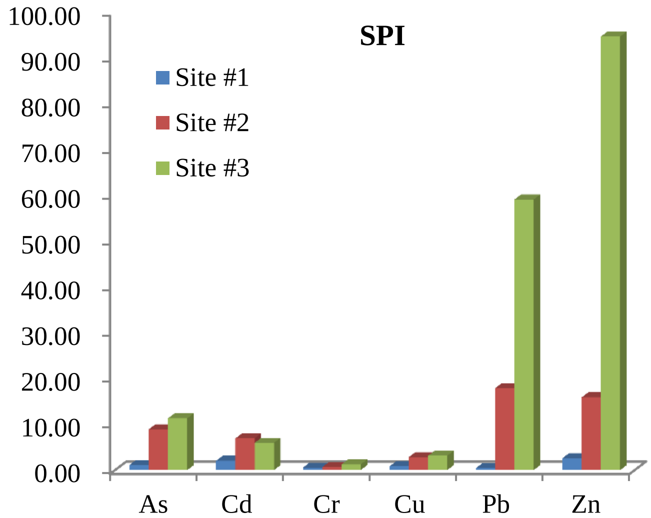

Fig. 2. Single pollution index of heavy metals at three sites

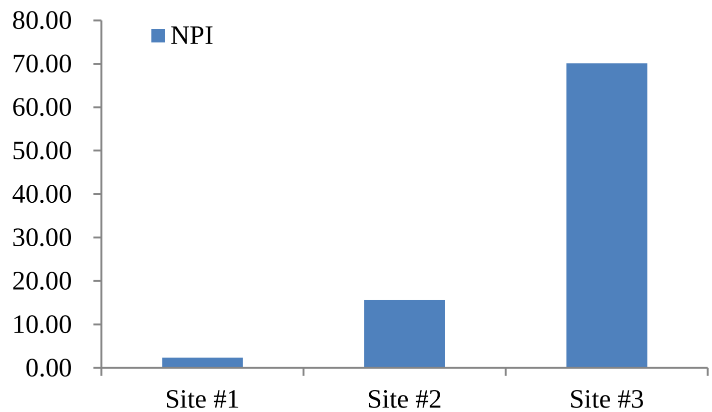

Fig. 3. Nemerow pollution index of heavy metals at three sites

The analysis result shows that the SPI of six heavy metal elements at site #1 decreased in the order Zn, Cd, As, Cu, Cr, Pb. Using SPI as a valuation criteria, in site #1 Pb, Cr and Cu belong to clean, As belongs to slight pollution grade, Cd and Zn belong to medium pollution grade. The value of NPI at Site #1 is 2.35 which is medium polluted through the valuation criteria shown in Table 1. The SPI of six heavy metal elements in site #2 decreased in the order Pb, Zn, As, Cd, Cu, Cr. The value of NPI at Site #2 is 15.61 which suggests that site #2 is serious polluted through the valuation criteria shown in Table 1. Taking SPI as a valuation criteria, in site #2, Cr belong to clean, As, Cd, Pb, Zn belong to serious contaminated. The SPI of six heavy metal elements at site #3 decreased in the order Zn, Pb, As, Cd, Cu, Cr. With SPI as valuation criteria, in site #3, Cr belong to slightly polluted, Cu belong to medium polluted, As, Pb, Zn belong to serious contaminated. The value of NPI at Site #2 is 70.09 which suggests that site #3 is serious polluted through the valuation criteria shown in Table 1. This study shows that site #2 and #3 need to control the soil pollution and promote ecological restoration (Wang et al., 2014).

4. Conclusion

(1) The As, Cd, Pb, Zn concentration of surface soil at control site #1 are slight above the soil background value of Hebei province; the total As, Cd, Cu, Pb, Zn concentration of surface soil at site #2 are 31.82, 1448.40, 7.20, 318.23, 88.64 times respectively as high as the soil background value of Hebei province；The Pb, Zn concentration of surface soil at site #3 exceed the background value seriously which value surpass 2×10^4 mg/kg。

(2) According to the Single Pollution Index assessment, Pb, Cr and Cu belong to clean scale, As belongs to slightly polluted scale, Cd and Zn belongs to medium polluted scale; At site #2, the concent of Cr belongs to clean, Cu belongs to slightly polluted, Cd, As, Zn and Pb belongs to heavy polluted, especially Pb is the most serious polluted. At site #3, Cr belongs to slightly polluted, Cu belongs to medium polluted, As, Pb, Zn belongs to heavy polluted, especially Zn is the most serious polluted.

(3) According to the Potential ecological Risk Index assessment, site #1 belongs to slightly ecological risk scale; the mean value of *RI* at site #2 is 245.1, which belongs to medium ecological risk scale; the mean value of *RI* at site site #3 is 393.5, which belongs to strong risk scale.

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