Distribution and Risk Assessment of Some Heavy Metal Elements in the Contaminated soil from Baiyin City, Gansu Province

Wan-Jiang Li¹, Zhuo-Xin Yin¹, Bin Yue¹, Tian-peng Gao¹,²* and Guo-Hua Chang¹

¹ College of Geography and Environmental Engineering, Lanzhou City University, Engineering Center for Pollution Control and Ecological Restoration in Mining of Gansu Province, Lanzhou 730070, China
² College of Biological and Environmental Engineering, Xi'an University, Xi'an 710065, China

Abstract. According to relevant standards and methods, ecological risk assessment and source analysis of 7 heavy metals (Ni, Cu, Zn, Cr, Cd, Pb and Hg) in the area Dongdagou of Baiyin were carried out. The results showed that the order of the average content of heavy metals in the soil in the sampling area was Zn > Cu > Pb > Cd > Cr > Ni > Hg. Among them, Zn, Cu and Pb have got unacceptably high levels, and the content of Cd was moderately exceeded. The order of the coefficient of variation of metals was Zn > Cd > Cu > Hg > Pb > Ni > Cr; soil pollution was characterized by compound pollution; the potential ecological risk coefficient of heavy metals was Hg > Cd > Cu > Pb > Zn > Ni > Cr. The comprehensive evaluation of potential ecological hazards of heavy metals showed that heavy metal pollution in the entire study area constituted a high-intensity ecological hazard. Therefore, the control of heavy metal pollution in the soil needs to be further strengthened.

1. Introduction
The pollution of heavy metals in soil is one of the most severe environmental problems in the world. At present, the total amount is mostly used as the benchmark for soil heavy metal pollution evaluation in actual practice [1-4]. With the development of China’s economy, the heavy metal pollution of soil is also an environmental issue that attracts most attention [5]. The main environmental effect of soil heavy metal pollution is the migration and accumulation of heavy metals from the soil to the plants, and the potential threat to human health through the action of the food chain [6]. Some researches in recent years [7, 8] indicate that the content of heavy metals in the soil system will affect its environmental behaviour and ecological effects. In soil pollution, the pollution caused by mining activities is the most serious ecological damage and environmental pollution problem [9]. Similarly, it is also one of the important sources of heavy metal pollutants in the soil [10]. In mining areas, a series of processing such as mining and metallurgy [11], transportation [12], and disposal of dump slag [13, 14] may cause the release and migration of various heavy metal elements and do harm to the surrounding soil environment. In recent years, soil heavy metal pollution caused by mining activities and the consequent risks of environmental and human health have attracted widespread attention from domestic and foreign researchers [10, 15, 16].

2. Methods and Materials
2.1. Regional Overview
Baiyin city is located in the upper reaches of the Yellow River and the central part of Gansu Province. The geographical position is between 103°3′-105°34′ east longitude and 35°33′-37°38′ north latitude. The altitude of the whole territory is between 1275-3321 m. The city is divided into three climate zones from south to north with aridity between 1.0 and 1.5. It is a semi-arid area with four distinctive seasons. Baiyin is a concentrated production area of non-ferrous metals copper, lead, zinc and the associated minerals. There are 45 kinds of rare metal minerals that have been discovered or proven in this place.

2.2. Sample Collection and Treatment
The sampling points were set up in 11 areas including the mine industrial zone, smelter in Dongdagou and surrounding places near the Yellow River port. Based on the sampling method, the samples were carried out from three stages at different depths. A total of 32 samples were collected, and the sampling points, shown in Figure 1, were accurately located by GPS. After the collected soil samples were sieved and mixed uniformly, the samples were prepared by a quarter method, and they were transported back to the laboratory to be air-dried, ground, and passed through a 100-mesh sieve for further preparation before analysis and testing. The contents of Ni, Cu, Zn, Cr, Cd and Pb in the samples were measured by atomic absorption spectrophotometry, and the content of Hg was measured by ICP-OES. The samples were tested in parallel for 4 times to control the quality of the analysis results.

![Figure 1. Schematic diagram of sampling points](image)

2.3. Assessment Method of Heavy Metal Pollution
2.3.1. Single Factor Pollution Index Method (PI) and Nemerow Multi-Factor Index Method (PN). In this paper, the single factor pollution index method (PI) is used to evaluate the pollution degree of heavy metals. The formula is as follows:

\[ PI_i = \frac{C_i}{C_s} \]  

Where, \( C_i \) represents the actual measurement of the \( i \)th polluted element in the soil; and \( C_s \) represents the evaluation standard concentration value of the \( i \)th polluted element in the soil. The Nemerow Integrated Pollution Index (PN) reflects the effects of pollutants on the soil. In the meantime, it highlights the effects of high levels of pollutants on the quality of the soil environment. The criteria for evaluating soil pollution in Nemerow Multi-factor Pollution Index are shown in Table 1.

| Level | Nemerow Multi-Factor Pollution Index | Pollution Degree(Safety Level) |
|-------|--------------------------------------|------------------------------|
| I     | \( PN \leq 0.7 \)                    | clean (safe)                 |
| II    | \( 0.7 < PN \leq 1.0 \)             | slight cleaning (warning limit) |
| III   | \( 1.0 < PN \leq 2.0 \)             | mild contamination           |
| IV    | \( 2.0 < PN \leq 3.0 \)             | medium pollution              |
| V     | \( PN > 3.0 \)                      | heavy pollution               |

2.3.2. Pollution Load Index (PLI) PLI is obtained as a concentration factor for each heavy metal relative to the soil background value. Metal contamination can be estimated. Thomilson et al. put forward the Pollution Load Index (PLI), which is used to detect pollution and compare pollution levels at different locations and different times. The formula of pollution load index (PLI) is as follows:

\[ PLI = \sqrt[\text{n}]{CF_1 \times CF_2 \times CF_3 \times \cdots \times CF_n} \]  

Where, \( CF \) represents the pollution factor and \( n \) represents the amount of metal. PLI greater than 1 indicates contaminated, while less than 1 indicates non-polluting.

2.3.3. Potential Ecological Risk Index (RI). The present study uses Hakanson’s Potential Ecological Risk Index (RI) to evaluate the potential ecological risks of heavy metals in soil, and the calculation formula is as follows:

\[ RI = \sum_{i=1}^{N} E_i = \sum_{i=1}^{N} \frac{T_{i} C_i}{C_s} = \sum_{i=1}^{N} \frac{T_{i}}{C_s} C_i \]  

In the formula, \( RI \) is a comprehensive potential ecological risk index for a variety of heavy metals in the soil, \( E_i \) is the potential ecological risk coefficient of the \( i \)th heavy metal. \( T_{i} \) is the toxicity coefficient of the \( i \)th heavy metal element, reflecting the toxicity level of heavy metals and the sensitivity of organisms to heavy metal pollution. \( C_i \) is the pollution factor for the \( i \)th heavy metal element, or to say, the pollution accumulation index of the \( i \)th heavy metal element. \( C_s \) is the measured value of heavy metal elements in soil, and \( C_{si} \) is the local soil background value. The greater the concentration of heavy metals is in the soil, the more types of the heavy metal pollutants are, and the higher the toxicity level of heavy metals is, the greater the \( RI \) value of the potential ecological risk index is, indicating the higher the potential ecological risk. The specific classifications can be seen in Table 2.

| Potential Ecological Risk | Low | Medium | High | Very High | Extremely High |
|--------------------------|-----|--------|------|-----------|---------------|
| \( E_i \)               | < 40| 40 ~ 80| 80 ~ 160| 160 ~ 320 | > 320         |
| \( RI \)                | < 150| 150 ~ 300| 300 ~ 600| 600 ~ 1200 | > 1200        |

3. Results and Discussions
3.1. Characteristics of Soil Heavy Metal Content

After analyzing the soil in the sample areas of the Dongdagou in Baiyin, the heavy metal concentration and its statistical analysis are shown in Figure 2.

The average value order of the heavy metal content of the soil in the sampling area is Zn > Cu > Pb > Cd > Cr > Ni > Hg. The coefficients of variation are in the order of Zn > Cd > Cu > Hg > Pb > Ni > Cr. The coefficients of variation of Pb, Ni and Cr are relatively small as 70.13%, 33.77%, and 33.24%, while the other four elements Zn, Cd, Cu, and Hg are significantly richer in the studied area and reach more than 90%, reflecting the distribution of these elements between the soils has great fluctuation. The pollution of the unexploited area is the lightest, thus it can be seen that smelter waste is the direct cause of the serious pollution in the area.

3.2. Factor Analysis of Heavy Metals in Soils

The characteristic values and cumulative contribution rates of factor analysis are shown in Table 3 with the factor analysis of the seven heavy metal element indicators of Zn, Cr, Cu, Pb, Cd, Ni and Hg. As can be seen from Table 3, under the premise of the cumulative variance of 69.800%, the analysis obtains two main component factors. Factor 1 (F1) and Factor 2 (F2), which can explain the 69.800% of the original data information, corresponding the principle of factor analysis. It can be seen from Table 3 that the total cumulative contribution rate before and after rotation has not changed with no loss in the total information. After rotation, the contribution rate of factor 1 is 49.905%, and the contribution rate of factor 2 (F2) is 19.896%. The variance rate of these two main component factors is only F1 in more than 40%, so factor 1 may be the most important source of soil heavy metal pollution in Dongdagou of Baiyin.
Table 3. Explanation of total variance analysis of heavy metal element factors in Dongdagou.

| Component | Initial eigen values | Extraction sums of squared loadings | Rotation sums of squared loadings |
|-----------|---------------------|------------------------------------|----------------------------------|
|           | Total               | % of variance | Cumulative % | Total               | % of variance | Cumulative % | Total               | % of variance | Cumulative % |
| F1        | 3.689               | 52.707       | 52.707       | 3.689               | 52.707       | 52.707       | 3.493               | 49.905       | 49.905       |
| F2        | 1.197               | 17.094       | 69.800       | 1.197               | 17.094       | 69.800       | 1.393               | 19.896       | 69.800       |
| F3        | 0.870               | 12.431       | 82.231       | 0.870               | 12.431       | 82.231       | 0.532               | 3.940        | 99.725       |
| F4        | 0.532               | 7.606        | 89.838       | 0.532               | 7.606        | 89.838       | 0.416               | 5.948        | 95.786       |
| F5        | 0.416               | 5.948        | 95.786       | 0.416               | 5.948        | 95.786       | 0.276               | 3.940        | 99.725       |
| F6        | 0.276               | 3.940        | 99.725       | 0.276               | 3.940        | 99.725       | 0.019               | 0.275        | 100.000      |

In factor analysis, it is helpful to better understand the meaning of the factor by rotating the orthogonal variance maximum. The results of the factor load matrix output before and after the rotation are shown in Table 4. As can be seen from Table 4, there is a big difference between the factor matrix after rotation and the factor matrix before the rotation, and the load on the rotated factor is obviously polarized to 0 and 1. The orthogonal factor solution shows that the factor F1 is a combination of Zn, Cr, Cu and Pb, and the concentration of these four elements has a high positive load on the factor, and the corresponding factor load values are 0.933, 0.912, 0.851 and 0.782, which reflects their rich characteristics. In Factor 2, the high load indicators are Ni and Hg, and the corresponding factor load values are 0.790 and 0.769 respectively. From Zn, Cr, Cu and Pb’s contribution to factor 1, it can be seen that Factor 1 (F1) mainly reflects the situation of mining activities in the Dongdagou, and it is called as “industrial and mining pollution factor”. In the contaminated area, the content of Cd, Ni and Hg is only the accumulation of higher concentration near the pollution sources of industrial and mining enterprises, while in other regions the spatial distribution is more uniform. The concentration varies little, so factor 2 is regarded as the urban factor.

Table 4. Factor loading matrix before and after rotation.

| Factor | Factor loading matrix before rotation | Factor loading matrix after orthogonal rotation of maximum variance |
|--------|--------------------------------------|---------------------------------------------------------------|
|        | F1                                   | F2 | F1 | F2 |
| Zn     | 0.934                               | -0.131 | 0.933 | 0.136 |
| Cr     | 0.916                               | -0.116 | 0.912 | 0.146 |
| Cu     | 0.885                               | -0.005 | 0.851 | 0.243 |
| Pb     | 0.805                               | -0.036 | 0.782 | 0.191 |
| Cd     | -0.527                              | 0.367    | -0.609 | 0.204 |
| Ni     | 0.173                               | 0.773    | -0.051 | 0.790 |
| Hg     | 0.489                               | 0.658    | 0.284 | 0.769 |

3.3. Assessment of Soil Heavy Metal Pollution
The results of pollution indexes of seven heavy metal at sampling points in the study area, are shown in Table 5. As can be seen from Table 5, in terms of the average single-factor pollution index of each element, surface soil is heavily polluted by heavy metals. Except for the single-factor pollution index of Cr and Ni that is less than 1, the rest are greater than 1. Cd, Hg and Zn are heavy pollution and their indexes reach 95.662, 8.871 and 5.195 respectively. The 7 heavy metal pollution levels range from high to low as Cd > Hg > Zn > Cu > Pb > Cr > Ni. The PLI is 711876.94, indicating that the study area is heavily polluted.
Table 5. Pollution index of heavy metals in soil.

| Elements | PI   | PLI  |
|----------|------|------|
|          | Minimum | Maximum | Mean |          |
| Zn       | 0.107  | 37.269 | 5.195 |          |
| Cr       | 0.116  | 0.518  | 0.312 |          |
| Cu       | 0.028  | 7.952  | 1.874 |          |
| Pb       | 0.295  | 3.506  | 1.424 |          |
| Cd       | 29.294 | 609.113| 95.662|          |
| Ni       | 0.058  | 0.309  | 0.166 |          |
| Hg       | 1.667  | 29.167 | 8.871 |          |

Based on the assessment method of potential ecological hazard index (RI), the results of $E_i^s$, a single coefficient of potential ecological hazards of 32 soil samples in Dongdagou district are shown in Table 6. The order of the $E_i^s$ of the seven heavy metals in Dongdagou soil is Hg (26612.90) > Cd (24740.10) > Cu (107.10) > Pb (101.71) > Zn (37.48) > Ni (4.35) > Cr (2.67). Among them, Hg and Cd’s $E_i^s$ are at considerable risk level; Cu and Pb are moderate risk; and Ni, Zn and Cr are low risk. According to the potential hazard coefficient of heavy metals in soil, the potential ecological risks of Ni, Zn and Cr are at the lowest hazard level and thus will not be harmful to agriculture or plant and animal growth for the time being. Hg and Cd are the most ecologically hazardous, and their contribution to the overall potential ecological hazard index is the largest. The average value of the comprehensive ecological Hazard Index (RI) for the entire study area was 3440.42 (Table 6), indicating that heavy metal pollution in the area has constituted high-intensity ecological hazards.

Table 6. Comprehensive ecological hazard index of heavy metal in soil.

| Elements | Potential ecological hazard coefficient of single factor ($E_i^s$) |
|----------|---------------------------------------------------------------|
|          | Zn  | Cr  | Cu  | Pb  | Cd  | Ni  | Hg  |
| Average Value | 37.48 | 2.67 | 107.10 | 101.71 | 24740.10 | 4.35 | 26612.90 |
| Range    | 0.77-268.90 | 0.99-4.44 | 1.62-21.10 | 21.10-7575.97 | 454.41-157529.10 | 1.53-8.10 | 5000.00-87500.00 |

4. Conclusion

(1) The average contents of the heavy metal elements in soil is Zn > Cu > Pb > Cd > Cr > Ni > Hg. And the coefficients of variation of the above metals are in order of Zn > Cd > Cu > Hg > Pb > Ni > Cr. Among them, Zn, Cd, Cu, and Hg have a coefficient of variation of more than 90%, reflecting the large volatility of the distribution of these elements between soils, which is largely caused by human industrial activity.

(2) In the soil of Dongdagou in Baiyin, heavy metal pollution shows the characteristics of compound pollution. Among them, Zn, Cr, Cu and Pb’s combination Factor 1 (F1) is the main factor of pollution, known as industrial and mining pollution factor. Which indicates their rich characteristics and also reflects that the mining activities in Dongdagou area has caused the higher accumulation of heavy metal content; whereas the concentration varies little in non-mining areas, and the mild pollution caused by Factor 2 may be caused by man-made activities.

(3) The potential ecological risk factors of the seven heavy metals are in the order of Hg > Cd > Cu > Pb > Zn > Ni > Cr. Hg and Cd are the most ecological hazardous, and their contribution to the total potential ecological hazard index is also the largest. The potential ecological risks of Ni, Zn and Cr are at the lowest harmful level. The comprehensive assessment of potential ecological hazards of heavy metals shows that there is a high-intensity ecological hazard risk in the soil area of Dadonggou, and it is imperative to implement the prevention and control of heavy metal pollution in the soil.
Acknowledgments
The research was funded by the National Natural Science Foundation of China (31860176), the Research Project of Universities in Gansu (2019B-169 and 2020A-124) and Doctoral Research Initiation Fund of Lanzhou City College (LZCU-BS2019-26).

References
[1] Liu W, Zhao J and Yang Z 2005 Impacts of sewage irrigation on heavy metal distribution and contamination in Beijing, China. Environment International. 31 805-812.
[2] Huang S S, Liao Q L and Hua M 2007 Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China. Science Direct. 67 2148-2155.
[3] Li Y X, Xu L C and Xiong X 2007 The spatial structure feature of heavy metals in agricultural soil of mining city: a case study of Fuxin, China. Acta Scientiae Circumstantiae. 27(4) 679-687.
[4] Marjia R and Davor R 2003 Heavy metals distribution in agricultural top soils in urban area. Environmental Geology. 43 795-805.
[5] Zhou J J, Zhou J and Feng R G 2014 Status of China's heavy metal contamination in soil and its remediation strategy. Bulletin of the Chinese Academy of Sciences. 29(3) 315-320.
[6] Zhao H R, Xia B C and Fan C 2012 Human health risk from soil heavy metal contamination under different land uses near Dabaoshan Mine, Southern China. Science of the Total Environment. 1(417-418) 45-54.
[7] Ramos L, Hernandez L M and Gonzalez M J 1994 Sequential fractionation of copper, cadmium and zinc in soil from or near Donana Nation Park. Journal of Environment Quality. 23 50-57.
[8] Liu Q, Wang Z J and Tang H X 1996 Research progress in heavy metal speciation and toxicity and bioavailability of heavy metals. Environmental Science. 17(1) 89-92.
[9] Pu C J, Qin D X and Li Y S 2004 Discussion on issues related to mining development and ecological environment. China Mining Magazine. 1(6) 23-26.
[10] Silva E F D, Zhang C and Pinto L S 2004 Hazard assessment on arsenic and lead in soils of Castromil gold mining area, Portugal. Applied Geochemistry. 19(6) 887-898.
[11] Vassilev S V, Eskenazy G M and Vassileva C G 2001 Behaviour of elements and minerals during preparation and combustion of the Pernik coal, Bulgaria. Fuel Processing Technology. 72(2) 103-129.
[12] Liao G L and Wu C 2005 Polluted characteristics of Zn, Pb, Cd, Cu and As in soil of different mining activity zones. Environmental Science. 1(3) 157-161.
[13] Licskő I, Lois L and Szebényi G 1999 Tailings as a source of environmental pollution. Water science & Technology. 39(10-11) 333-336.
[14] Dang Z, Liu C and Haigh M J 2002 Mobility of heavy metals associated with the natural weathering of coal mine spoils. Environmental Pollution. 118(3) 419-426.
[15] Yang Q W, Shu W S and Qiu J W 2004 Lead in paddy soils and rice plants and its potential health risk around Lechang Lead/Zinc Mine, Guangdong, China. Environment International. 30(7) 883-889.
[16] Xie H, Liao X Y, Chen T B and Lin J Z 2005 Arsenic in plants of farmland and its healthy risk: a case study in an As-contaminated site in Dengjiatang, Chenzhou City, Hunan province. Geographical Research. 24(1) 371-375