Ecological risk assessment of heavy metals in soils around mining area: comparison of different assessment methods

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Abstract: The farmland soil around the mercury mining area of Xunyang mansion was investigated and analyzed, and different methods were used to evaluate the soil. The results show that the contents of chromium, nickel, cadmium and mercury in Gongguan mercury mining area are 97-1113 mg / kg, 76-601 mg / kg, 0.415-1.458 mg / kg, 1.050-5.273 mg / kg, all of which exceed the standard values. The results show that the mercury pollution in Gongguan mercury mining area is extremely serious; the Nemer pollution index method shows that the soil near the Gongguan mercury mining area has been polluted in different degrees, and the crops near the mining area have the tendency to pollute heavy metals; the potential ecological risk index method shows that the heavy metal mercury in Gongguan mercury mining area presents a very strong risk level. The evaluation results of different evaluation methods are quite different. Therefore, in the follow-up evaluation, the appropriate evaluation method should be selected according to the purpose of evaluation.

1. Introduction

Soil is one of the most important geographical elements in nature and the material basis for human survival and development[1]. In recent years, with the deepening of urbanization and industrialization in China, a large number of toxic and harmful substances are released into the soil environment, which poses a serious threat to the soil environment[2]. According to the national soil pollution survey bulletin issued by the Ministry of environmental protection on April 17, 2014, more than 19% of arable land soil in China has been polluted by heavy metals to varying degrees, which are mainly from sewage irrigation and industrial activities, among which mining, transportation, smelting, refining and other activities are the main causes of heavy metal pollution[3]. The pollutants such as waste water, waste gas and waste residue produced in mining and smelting process are released and transferred through environmental media, causing the soil, water body and crop heavy metals near the mining area to seriously exceed standards [4-5]. The heavy metals in the soil are persistent, hard to decompose, toxic and hidden. The heavy metals hidden in the soil inhibit the soil function, poison the soil microorganisms and plants, thus endangering the whole food chain[6]. Nowadays, the pollution
of heavy metals in the soil near the mining area has aroused widespread concern\(^\text{[7-8]}\). Research shows that due to mining and smelting in the mining area, water \(^\text{[9]}\), soil and crops \(^\text{[10-11]}\) near the mining area are polluted by heavy metals to varying degrees.

Based on the investigation and analysis of the heavy metal content in the surrounding soil of Gongguan mercury mine in Xunyang County, this paper uses the land cumulative pollution index method, the Nemero comprehensive pollution index method and the potential ecological harm index method to evaluate the status of heavy metal pollution and ecological risk in the soil, and analyzes the advantages and disadvantages of different methods. It is the evaluation of heavy metal pollution in the surrounding soil of Xunyang mercury mine to prevent and control heavy metal pollution in time. The metal mining process provides scientific basis for the pollution of the surrounding environment.

2. Materials and methods

2.1 Soil collection and measurement

The soil samples were collected from the surrounding area of Gongguan mercury mine, Xunyang County, Ankang City, Shaanxi Province, and the soil collection was carried out in November 2017. According to the requirements of the technical code for soil environment monitoring, the sampling point collects the surface soil (0-20 m) of the nearby farmland in the form of "s" point distribution. After the sample collection, it is put into a plastic bag, labeled and brought back to the laboratory. The soil sample is dried under the natural conditions, the foreign matters are removed, grinded through 0.149 mm sieve and mixed for standby\(^\text{[12]}\). Determination of copper, lead, nickel, zinc, cadmium, chromium and arsenic in soil samples by ICP-MAS (Agilent 7700) after digestion with HNO$_3$-HClO$_4$-HF\(^\text{[13]}\), The mercury in the soil sample was digested by HNO$_3$-H$_2$SO$_4$, and the supernatant was determined by atomic fluorescence spectrometer (AFS-9760) \(^\text{[14]}\).

2.2 Evaluation of land cumulative pollution index method

$I_{geo}$, known as Muller index, is a quantitative index proposed by German scientist Muller \(^\text{[15]}\) in the late 1960s and developed in Europe to study the pollution degree of heavy metals in sediments and other substances. The expression is as follows:

$$I_{geo} = \log_2 \left( \frac{C_i}{K B_i} \right)$$

Where: $I_{geo}$ is the cumulative land pollution index; $C_i$ is the measured mass concentration of heavy metal $i$; $B_i$ is the environmental background value of the measured elements (in this study, the soil background value of Shaanxi Province is selected, see Table 2), $K$ is the correction coefficient, generally $K = 1.5$. According to the cumulative pollution index, the pollution degree of heavy metals can be divided into 7 grades, see Table 1 for details.

| $I_{geo}$ | Level | Pollution level               |
|---------|-------|--------------------------------|
| $I_{geo} < 0$ | 0     | Pollution-free                |
| $0 \leq I_{geo} < 1$ | 1     | Light medium pollution        |
| $1 \leq I_{geo} < 2$ | 2     | Moderate pollution            |
| $2 \leq I_{geo} < 3$ | 3     | Medium strong pollution       |
| $3 \leq I_{geo} < 4$ | 4     | Strong pollution              |
| $4 \leq I_{geo} < 5$ | 5     | Strong extremely serious pollution |
| $I_{geo} \geq 5$ | 6     | Very serious pollution        |
Table 2 Environmental background values and toxic-response parameters of heavy metals in the soils

| Element | Cd (mg/kg) | Cr | Hg | As | Pb | Cu | Zn | Ni |
|---------|------------|----|----|----|----|----|----|----|
| c_i     | 0.76       | 62.5 | 0.063 | 11.1 | 21.4 | 21.4 | 69.4 | 28.8 |
| C_i     | 30         | 2   | 40  | 10  | 5  | 5  | 1  | 5  |

2.3 Nemero comprehensive pollution index method

The Nemero index is proposed by the American scholar Nemero in the book "scientific analysis of river pollution". At present, this method is one of the most commonly used methods for comprehensive pollution index at home and abroad. In this method, the sub index of each factor (multiple of exceeding standard) is calculated first, then the average value of sub index is calculated, and the maximum sub index and average value are calculated.

(1) Single factor index method

Through single factor evaluation, the main heavy metal pollutants and their harm degree can be determined. Generally, the pollution index is expressed by pollution index, and the pollution index is calculated by comparing the measured value of heavy metal content with the removal dimension of evaluation standard. The calculation formula is as follows:

\[ P_i = \frac{C_i}{S_i} \]  

Table 3 Soil single pollution level grading standard

| Pollution level     | P_i≤1 | 1<P_i≤2 | 2<P_i≤3 | P_i>3 |
|---------------------|-------|---------|---------|-------|
| Pollution-free      |       |         |         |       |
| Light pollution     |       |         |         |       |
| Middle pollution    |       |         |         |       |
| Heavy pollution     |       |         |         |       |

(2) Composite index method

The single factor index can only reflect the pollution degree of single heavy metal element, and cannot comprehensively reflect the pollution status of soil, while the comprehensive pollution index takes into account the average value and the highest value of single factor pollution index, which can highlight the role of heavy metal pollutants. The calculation method of comprehensive pollution index is as follows:

\[ P_z = \sqrt{\frac{(P_i)^2 + P_{i\text{max}}^2}{2}} \]

Where: P_z is the comprehensive pollution index of the sampling point; P_{i\text{max}} is the maximum of the single pollution index of heavy metal pollution of the sampling point i; \( \bar{P} = \frac{1}{n} \sum_{i=1}^{n} P_i \) is the single factor index average. See Table 4 for the classification standard of comprehensive pollution index.

Table 4 Soil comprehensive pollution degree grading standard

| Soil comprehensive pollution level | Soil comprehensive pollution index | Pollution level | Contamination level |
|-----------------------------------|------------------------------------|----------------|--------------------|
| 1                                 | P_i≤0.7                            | security       | clean              |
| 2                                 | 0.7<P_i≤1.0                        | Cordon         | Still clean        |
| 3                                 | 1.0<P_i≤2.0                        | Light          | When the pollutant exceeds the initial |
pollution pollution value, the crop begins to pollute

| 4 | 2.0 < $P_z \leq 3.0$ | Middle pollution value | Serious soil and crop pollution |
|---|----------------------|------------------------|--------------------------------|
| 5 | $P_z > 3.0$          | Heavy pollution value   | Serious soil and crop pollution |

### 2.4 Evaluation of Potential Ecological Hazard Index Method

Potential ecological risk index method was proposed by Lars Hakanson [16], a famous geochemist in Sweden, in 1980, also known as Hakanson index method, which was originally used to evaluate the potential ecological risk of toxicants in sediments and soil at the bottom of rivers and lakes. In recent years, nearly 90% of researchers use this method to evaluate the potential ecological risk of heavy metals in polluted soil. Its expression is as follows:

$$C_f^i = C^i_m / C^i_n$$

(4)

$$E^i_r = T^i_r \times C^i_f$$

(5)

$$RI = \sum E^i_r$$

(6)

In the formula: $E^i_r$ is the potential ecological hazard index of single heavy metal; $T^i_r$ is the toxicity response coefficient of a single heavy metal. In this study, standards formulated by Hakanson are mainly used, see Table 2 for details; $C^i_f$ is the pollution parameter of a heavy metal; $C^i_n$ is the corresponding evaluation standard of each element. In this study, soil background value of Shaanxi Province is selected, see Table 2 for details. $E^i_r$ describes the pollution degree of a single pollutant. $E^i_r$ can be divided into five grades from low to high. $RI$ describes the comprehensive value of potential ecological coefficients of multiple pollutants at a certain point, which is divided into four grades. See Table 5 for details.

#### Table 5 Potential Ecological Risk Grading Standards

| $E^i_r$ | $RI$ | Pollution level                      |
|---------|------|--------------------------------------|
| $E^i_r$ |      | Low ecological harm                  |
| 40 ≤ $E^i_r$ < 80 | 150 ≤ $RI$ < 300 | Moderate ecological hazard           |
| 80 ≤ $E^i_r$ < 160 | 300 ≤ $RI$ < 600 | Strong ecological harm               |
| 160 ≤ $E^i_r$ < 320 | $RI$ ≥ 600 | Strong ecological harm               |
| $E^i_r$ ≥ 320 |      | Extremely strong ecological harm      |

### 2.5 Data Statistics

The original 10.0 is used for drawing, and excel and SPSS are used for statistics and analysis of data.

### 3. Results and Discussion

#### 3.1 Heavy Metal Content in Soil

The contents of chromium, nickel, copper, zinc, arsenic, cadmium, lead and mercury in the soil near Gongguan mercury mining area are 97-1113 mg/kg, 76-601 mg/kg, 25-50 mg/kg, 99-310 mg/kg, 7-54 mg/kg, 0.415-1.458 mg/kg, 66.41-92.30 mg/kg, 1.050-5.273 mg/kg, respectively. Among them, the average content of chromium, nickel, cadmium, mercury and individual sampling points all exceed the screening value of agricultural land soil pollution risk (hereinafter referred to as the standard value) in Table 1 of standard for soil environmental quality control of agricultural land soil pollution risk (Trial) (gb15618-2018), with the average content of 380, 238, 0.756 and 3.858 mg/kg, respectively, which were 1.9, 1.2, 2.5 and 1.6 times of the standard value, and the weight was 1.9, 1.2, 2.5 and 1.6 times of the standard value. The over standard rates of chromium, nickel, cadmium and mercury were 66.7%, 33.3%, 100% and 66.7% respectively.
Table 6 Heavy metal content in mining area

| Sampling site                  | Number | Cr (mg/kg) | Ni | Cu | Zn | As | Cd | Pb | Hg |
|--------------------------------|--------|------------|----|----|----|----|----|----|----|
| Gongguan mercury mine G1      | 97     | 101        | 46 | 217| 54 | 1.458 | 91.59 | 5.273 |
| G2                            | 102    | 76         | 35 | 130| 15 | 0.850 | 67.27 | 7.571 |
| G3                            | 769    | 540        | 46 | 99 | 14 | 0.462 | 92.30 | 1.566 |
| G4                            | 1113   | 601        | 50 | 101| 22 | 0.526 | 67.57 | 1.050 |
| G5                            | 267    | 147        | 34 | 107| 7  | 0.674 | 66.41 | 2.735 |
| G6                            | 206    | 132        | 25 | 310| 12 | 0.415 | 74.75 | 4.950 |
| mean value                    | 380    | 238        | 38 | 152| 28 | 0.756 | 70.40 | 3.858 |

GB15618-2018

| Screening value | Control value |
|-----------------|---------------|
| ≤200            | ≤1000         |
| ≤200            | /             |
| ≤250            | /             |
| ≤30             | ≤120          |
| ≤0.3            | ≤3.0          |
| ≤120            | ≤700          |
| ≤2.4            | ≤4.0          |

3.2 Evaluation of land cumulative pollution index method

At present, the method of soil cumulative pollution index is widely used in soil environmental assessment at home and abroad. This method not only considers the influence of human factors on heavy metal pollution, but also takes into account the influence of soil environmental geochemical background value on heavy metal pollution. Figure 1 shows the evaluation results of the cumulative pollution of each mining area in the study area. According to the evaluation standard, cadmium in the soil of all sampling points of Gongguan mercury mine is not polluted, copper, zinc and arsenic are medium pollution, and chromium and nickel are medium strong pollution.

![Figure 1 evaluation results of cumulative pollution index](image)

3.3 Evaluation of Nemero pollution index

According to the grading standard of single pollution degree of soil (Table 3), Cu, Zn, as and Pb of Gongguan mercury mine are non pollution, Cr is light pollution, Ni and Hg are heavy pollution, Cd is medium pollution; according to the grading standard of comprehensive pollution degree of soil (Table 4), the surrounding soil of Gongguan mercury mine is light pollution, and crops are threatened by heavy metal pollution.

Table 7 Evaluation of Nemero pollution degree

| Sampling Site | \( P_i \) |
|---------------|---------|
| Gongguan mercury mine | Cr Ni Cu Zn As Cd Pb Hg |
|                | 1.16 5.32 0.39 0.64 0.69 2.44 0.26 7.72 1.98 |
3.4 Potential ecological pollution evaluation index method

Table 8 shows the evaluation results of ecological hazard index method and the proportion of $E_i$ in potential ecological hazard index $RI$. According to the classification standard of potential ecological risk, the mercury in Gongguan mercury mining area has reached a very strong level of ecological hazard (Table 3), the heavy metal nickel shows a medium level of ecological hazard, and the rest heavy metals are low level of ecological hazard; from Figure 2, it can be seen that the ecological hazard index of single heavy metal mercury in Gongguan mercury mining area accounts for 95.1% of $RI$. Therefore, the heavy metal mercury in the mercury mining area is the main cause of ecological harm in this area.

| Sampling Site | Heavy Metal | $E_i$/RI | $E_i$/RI |
|---------------|-------------|----------|----------|
| Gongguan mercury mine | Cr | Level A | 12.16 | 0.47 |
| | Ni | Level B | 41.32 | 1.60 |
| | Cu | Level A | 8.88 | 0.34 |
| | Zn | Level A | 2.19 | 0.08 |
| | Cd | Level A | 29.84 | 1.16 |
| | Pb | Level A | 16.45 | 0.64 |
| | As | Level A | 25.23 | 0.98 |
| | Hg | Level E | 2449.52 | 95.06 |
| RI | | | 2576.08 | |

3.5 Comparison of several evaluation methods

According to the evaluation of cumulative pollution index method, the mercury in Gongguan mercury mine is seriously enriched, the heavy metals chromium, nickel and lead are moderately polluted, and the rest heavy metals are light or non polluted; the potential ecological hazard index shows that the heavy metals nickel and mercury in Gongguan mercury mine are moderately and seriously polluted, respectively. As far as this study is concerned, the result of Nemero comprehensive pollution index method is better than that of cumulative pollution index method and potential ecological risk index method. The pollution of nickel, cadmium and mercury in the mercury mine of the mansion was severe moderate severe pollution. According to different soil pollution conditions, the results of different evaluation methods vary greatly. Therefore, in the follow-up evaluation, the appropriate evaluation method should be selected according to the purpose of evaluation.

4. Conclusion

The results show that the average content of heavy metals chromium, cadmium, mercury and nickel in Gongguan mercury mining area is higher than the screening value of agricultural land soil pollution risk (hereinafter referred to as the standard value) in Table 1 of soil environmental quality control standard for agricultural land soil pollution risk (Trial) (GB15618-2018). The potential ecological risk assessment shows that the soil near the mercury mine is at a very serious level of ecological risk, mainly due to the serious pollution of heavy metal mercury. In the future, we should pay more attention to the heavy metal pollution of farmland near the mining area, especially the heavy metals...
such as Hg, Cd, Pb and As.

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