Characteristics of Heavy Metal Pollution in Farmland Soil along the Lancang River in Lincang, Yunnan

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Abstract. Taking the farmland soil along the Lancang River in Lincang as the research object, through soil sampling test and analysis, using single factor evaluation method, Nemeiro comprehensive pollution index method and relative pollution index method, the heavy metals As, Cd, Pb and Zn pollution characteristics and causes in farmland along the Lancang River were analyzed. The results show that according to the national soil environmental quality standards, the Cd in the farmland along the Lancang River in Lincang seriously exceeded the standard on a large scale, followed by Pb and Zn, while As did not exceed the standard; the soil single factor pollution index is Cd>Zn>Pb>As. It shows that the relative pollution indexes of As, Cd, Pb and Zn in farmland soil all exceed the standard, and the exceeding rate is Pb>Zn>Cd>As. The pollution of heavy metals in the soil of the farmland along the Lancang River in Lincang is not only caused by mine development, but also related to its high background value. The pollution of heavy metals in farmland soil along the north river from upstream to downstream has changed significantly. The correlation between the pollution of As, Cd, Pb and Zn in the farmland along the Lancang River in Lincang is significant, the probability of homology is very high, and there is a danger of combined pollution of four heavy metals.

Keywords: Lancang River, heavy metal pollution, pollution index, compound pollution

1. Introduction
The upper and middle reaches of the Lancang River refers to the section from Tibet that enters Deqin and Weixi counties in Diqing Prefecture, Yunnan Province, to Gongcrossing the bridge in Lanping County, with a flow of 460 km and a basin area of 1190 square kilometers. The industrial development of the upper and middle reaches of the Lancang River mainly relies on the production and development of mineral resources [1]. Among them, the development of mineral resources is mainly in Lanping County, Nujiang Prefecture. The research targets are mainly concentrated in 5 mining areas in the upper and middle reaches of the Lancang River. At the same time, we select residential areas more than 1 km downstream of each mining area to study the content of heavy metals in the soil, and select Lajing Town, where no minerals are mined in this watershed, as the control area [2]. A large amount of water quenching slag, tailings and acid sludge are produced every year in the mining area of the river basin but not properly treated. After being washed by rain, heavy metals such as As, Zn, Cd,
Pb and their acidic substances in the waste slag will enter the rice field with the rain. soil. Over the past few decades, heavy metal pollution in rice fields and corn fields has been caused, which has affected the local agricultural economy and farmers' living standards and health [3].

2. Experimental program

2.1 Soil sample collection
Based on GPS point selection and positioning, 39 farmland soil samples with a soil depth of 10-20 cm were collected on both sides of the Lancang River section. Digging pits for sampling, take 1 kg of soil samples from each of the five quincunx-shaped pits, mix them diagonally, bring them back to the laboratory, and place them in a ventilated indoor place to dry naturally. The air-dried soil sample is crushed, sieved, and bagged for analysis of the total amount of heavy metals As, Zn, Cd, Pb and soil pH. Since the farmland is mainly distributed along the banks of the Lancang River, and the Lancang River water has been used for irrigation in history, the selection of sampling points is limited to farmland within 200m along the bank of the Lancang River. The sampling density mainly considers the degree of influence of industry and mining and the size of farmland. In the upstream section, it is most affected by the development of minerals. The farmland area is wide and the distribution is relatively concentrated, and the sampling is dense; the middle and lower river valleys are cut deeper, and the farmland is only distributed in the relatively flat sections of the river, with a relatively small population and less industry and mining. The sampling is scattered. A total of 39 sample points were arranged, and these samples were divided into sections based on the distance between the sample points and the location of the upper and lower reaches of the mining area, combined with the upper, middle and lower reaches of the Lancang River.

2.2 Instrument
AA-6200 flame atomic absorption spectrophotometer, lead (Pb), cadmium (Cd), manganese (Mn) single element hollow cathode lamp (National Institute of Nonferrous Metals), electronic balance (sensitivity 0.1 mg) [4,5].

2.3 Reagents
Lead standard solution (1000 μg/mL), cadmium standard solution (1000 μg/mL), manganese standard solution (10 μg/mL) provided by the National Institute of Nonferrous Metals; nitric acid (HNO₃), perchloric acid (HClO₄), the reagents used are all premium grade pure, laboratory water is deionized water [6].

2.4 Utensils handling
Glass instruments use 65% nitric acid 769 mL plus 4231 mL deionized water to prepare 10% nitric acid 5000 mL. All glass instruments are soaked in 10% nitric acid for 24 hours, and then rinsed with deionized water after drying. be usable [7].

Polyethylene products are cleaned with detergent with a volume fraction of less than 1%, then rinsed with deionized water, and then rinsed with deionized water several times before collection.

2.5 Sample processing
According to the wet ashing method and FAAS method in the national standards for the determination of lead, cadmium, and manganese, use an electronic balance to weigh 1.00~5.00g sample into a 50 mL Erlenmeyer flask, acidify with 10 mL nitric acid overnight, place it on an electric heating plate and heat at high temperature until white smoke emerges, indicating that the sample has been completely dissolved and digested. Use a funnel with filter paper for the cooled digestion solution and transfer to a colorimetric tube, and dilute to 50 mL to be tested.
2.6 Determination of heavy metal content in samples
The content of lead, cadmium, and manganese in the sample to be tested is determined by atomic absorption spectrophotometry. Each element is determined by parallel samples and the average value is calculated [8].

3. Results and analysis

3.1 Analysis of the results and causes of excessive soil heavy metal content
1) The content of heavy metals in the soil exceeds the standard
The content exceeding standard was analyzed according to the secondary standard of "Soil Environmental Quality Standard" (GB15618-1995). After testing, the pH of all soil samples were in the range of 3.88 ~ 6.15, which was acid soil. The average values of As, Cd, Pb, and Zn exceeded the standard by 0.38, 67.33, 2.09, and 4.47 times respectively. The Cd content in 39 sampling points exceeded the standard, and the over-standard rate reached 100%; 22 sample points Zn exceeded the standard, and the over-standard rate reached 56.41%; 12 sample points Pb exceeded the standard at one sampling point, with an over-standard rate of 30.77%; As only two sampling points exceeded the standard with an over-standard rate of 5.13%. The exceeding rate of the four heavy metal elements is Cd>Zn>Pb>As.

2) The distribution characteristics and reasons of soil heavy metal content
SPSSI3.0 software was used to perform one-way ANOVA on the content of heavy metals in farmland soil. The results show that there is a significant difference between As, Cd, Pb and Zn at the level of 0.01. The coefficient of variation of the content of the four elements is generally higher, all above 100%, especially the coefficients of variation of Pb and Zn are as high as 294.12% and 194.16, respectively. The content of the four elements varies significantly between different sampling points, as shown in table 1.

| project | Content range mg/kg | Mean mg/kg | Over-standard samples / total samples | Over-standard rate % | Standard deviation | Coefficient of Variation % |
|---------|---------------------|------------|--------------------------------------|---------------------|---------------------|---------------------------|
| As      | 4.0-100             | 18         | 5/39                                 | 5.03                | 23                  | 130                       |
| Cd      | 3 -110              | 20         | 39/39                               | 98.00               | 30                  | 200                       |
| Pb      | 50-9000             | 500        | 22/40                               | 32.00               | 500                 | 125                       |
| Zn      | 60-7000             | 850        | 4/40                                | 56.00               | 630                 | 160                       |

3.2 Evaluation results and cause analysis of single factor index method and Nemeiro comprehensive pollution index method
1) Evaluation results of single factor index method
The calculation results of farmland soil single factor index in the study area are shown in Table 2 and Figure 1. Combining the single-factor pollution index method and the pollution degree classification standard, it can be seen that the farmland soil along the Lancang River is polluted by As, Cd, Pb and Zn in different degrees. Among them, Cd in the soil of all sampling points is extremely polluted, followed by Zn and Pb. The average pollution degree is heavy and moderate pollution respectively, and As pollution is the smallest, only 2 sampling points are moderately polluted, and the average pollution degree is not contaminated. The average value of single-factor pollution index is Cd>Zn>Pb>As, which is consistent with the ranking status of over-standard rate.
Table 2 pH, single factor pollution index, Nemeiro comprehensive pollution index and pollution level of each sampling point

| project            | pH  | Single factor pollution index | Nemeiro Comprehensive Pollution Index |
|--------------------|-----|-------------------------------|--------------------------------------|
|                    |     | As   | Cd  | Pb  | Zn  | P   |
| average value      | 5.0 | 0.5  | 67  | 2.0 | 4.5 | 49  |
| Maximum value      | 6.0 | 2.8  | 400 | 38  | 40  | 295 |
| Minimum value      | 4.0 | 0.1  | 13  | 0.1 | 0.3 | 9.6 |

Figure 1. Single factor pollution index curve of each heavy metal

2) Nemeiro comprehensive pollution index evaluation results

The calculation results of the Nemeruo comprehensive pollution index of farmland soil in the study area are shown in Table 3 and Figure 2 and 3. Combined with the Nemeiro comprehensive pollution index classification standard, it can be seen that the Nemeiro comprehensive pollution index of 39 sampling points is heavily polluted, with an average value of 46.39, which is far greater than the lower limit of the heavy pollution level (P>3). It is consistent with the distribution of the lowest point and highest point of the pollution index of Pcd in the single factor pollution index method. From the upper reaches of the Lancang River to the lower reaches of Nemelo, the comprehensive pollution index has changed significantly.

Figure 2. Nemeiro comprehensive pollution index for each sampling point
Figure 3. The average value of the comprehensive pollution index of each section

3.3 Analysis of evaluation results of relative pollution index method
It can be seen from Table 3 and Figure 4 that compared with the benchmark control values, the average relative pollution indexes of As, Cd, Pb and Zn in the farmland along the Lancang River are 1.37, 1.91, 4.19 and 3.31, respectively, and the exceeding rates are 43.24%, 45.95%, 59.46% and 48.65%, Pb>Zn>Cd>As. The reference control values of As, Cd, Pb and Zn in the soil exceed the national soil environmental background value by 1.47, 137.47, 5.00 and 4.12 times, of which the reference control value of Cd, followed by Pb, Zn and As, indicating that the pollution of As, Cd, Pb and Zn in the soil is not only caused by mine development, but also related to its high natural background value.

![Relative pollution index curve of various heavy metals](image)

Figure 4. Relative pollution index curve of various heavy metals

| Table 3 Relative pollution index status |
|----------------------------------------|
| element | Benchmark value | Relatively exceed the number of standards | National Soil Environmental Background Value | Relative pollution index maximum | Relative pollution index minimum | average value | Standard deviation |
|--------|-----------------|--------------------------------------------|---------------------------------------------|-------------------------------|-------------------------------|---------------|-------------------|
| As     | 14              | 15                                         | 10                                          | 7.8                           | 0.3                           | 1.3           | 1.6               |
| Cd     | 11              | 18                                         | 0.1                                         | 11                            | 0.4                           | 2.0           | 2.6               |
| Pb     | 130             | 21                                         | 26                                          | 73                            | 0.3                           | 4.0           | 13                |
| Zn     | 280             | 19                                         | 68                                          | 30                            | 0.2                           | 3.0           | 6.5               |

3.4 Analysis of characteristics of soil heavy metal compound pollution
Studying the correlation between heavy metal elements in the soil can infer whether the sources of heavy metals are the same. If there is a significant correlation between heavy metals, it means there may be the same source, otherwise the source may be different. It can be seen from Table 4 that the
correlation coefficients between As, Zn, Cd, and Pb in the farmland soil along the Lancang River are all high, all above 0.778, which is a significant correlation at the level of 0.01, indicating that As, Cd, Pb and Zn are in specific soils. There are mutual connections in the environment. The probability of homology is high, and the sources of the four elements are the same. The farmland along the Lancang River has compound pollution of 4 kinds of heavy metals to varying degrees. This is related to the long-term use of polluted Lancang River water for irrigation of farmland along the Lancang River and the direct pollution of acidic wastewater, slag, and dust from the mining area.

| element | Zn   | As   | Pb   | Cd   |
|---------|------|------|------|------|
| As      | -    | 1.00 | -    | -    |
| Pb      | 0.32 | 0.85 | 1.00 | -    |
| Cd      | -    | 0.90 | 0.93 | 1.00 |
| Zn      | 1.0  | 0.79 | 0.80 | 0.54 |

4. Conclusion
Studies have shown that in the farmland soil along the Lancang River, Cd is severely exceeded in a wide range, followed by Pb and Zn, while As does not exceed the standard. According to the national soil environmental quality standard, the average value of Cd exceeds the standard by 67.33 times, and the average value of Zn and Pb exceeds the standard 4.47 and 2.09 times, the exceeding rate of all soil samples is Cd>Zn>Pb>As.

The single factor index method evaluation results show that the farmland soil along the Lancang River is polluted by Cd, Pb, Zn and As. Among them, the soil at all sampling sites was extensively polluted by Cd, most of the farmland soil was heavily polluted by Zn, Pb pollution was moderately polluted, and As was only found in a few soils, and the average pollution degree was unpolluted. The average value of single factor pollution index is Cd>Zn>Pb>As.

The evaluation results of Nemeiro comprehensive pollution index show that the Nemeiro comprehensive pollution index of farmland soil along the Lancang River has reached the heavy pollution level, with an average value of 46.39, which is far greater than the lower limit of the heavy pollution level (P>3).

The relative pollution index evaluation results show that the benchmark control value of Cd in the study area is the highest, followed by Pb, Zn and As. The benchmark control values of As, Cd, Pb and Zn exceeded the national soil environmental background value by 1.47, 137.47, 5.00 and 4.12 times respectively. Compared with the reference value, the relative pollution index of As, Cd, Pb and Zn in the farmland along the Lancang River exceeded the standard, and the exceeding rate is Pb>Zn>Cd>As.

The analysis of the characteristics of soil heavy metal compound pollution shows that the correlation between As, Cd, Pb and Zn in the farmland along the Lancang River is significant, the probability of homology is high, and there is a risk of 4 types of heavy metal compound pollution.

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