

Analysis of Heavy Metal Pollution Characteristics of Agricultural Soils Around Polluted Rivers and its Correlation with River Sediments

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Abstract

To understand the characteristics of heavy metal pollution in farmland soils around Jiaozuo section of Jianggou River and its correlation with river sediments, 12 sediment samples from tributaries of Jianggou River and 18 soil samples from surrounding farmland were collected for the study, and the heavy metal contents of Cd, Cr, As, Pb, Hg, Zn, Cu and Ni in soil and sediment were determined. Based on the background values of soils in Henan Province and the screening values of soil pollution risk in agricultural land, the current situation and ecological risk of farmland soil pollution were analyzed and evaluated by using single factor index and Nemero index, and the correlation between heavy metals in farmland soil and river sediment was analyzed. The results showed that the average contents of eight heavy metal elements (Cd, Cr, As, Pb, Hg, Zn, Cu and Ni) in farmland soils were 1.49, 73.32, 10.76, 39.99, 0.05, 63.91, 62.15 and 43.17 mg/kg, respectively, and the average values of all heavy metals in farmland soils except Hg were higher than the Henan The mean values of heavy metals in agricultural soils, except Hg, are higher than the background values in Henan Province, and Cd, Cu and Ni have significant cumulative effects; while the mean values of heavy metals in river sediment, except Cr and Pb, are higher than the background values in Henan Province, and Cd, As, Zn and Ni have significant cumulative effects; the results of single factor index method, Nemero integrated pollution index method and integrated potential hazard risk index RI analysis show that Cd is the main pollution factor in agricultural soils and river sediment. Cd is the main pollution factor and has a strong risk of Cd pollution. The correlation analysis showed that the sources of Cd and As were similar and highly correlated with those in the river sediment; from the analysis, it was mainly from the irrigation of the surrounding rivers and the application of phosphorus fertilizer.

Keywords

Agricultural Soils; Heavy Metal Characteristics; Correlation; River Sediment; Ecological Risk Assessment.

1. Introduction

Heavy metal pollution of agricultural soils is becoming increasingly serious, and the contamination of soils with toxic and hazardous compounds leads to degradation or loss of soil functions[1]. Heavy metal elements are persistent, toxic, cumulative and hidden in agricultural soils[2], and the soil pollution caused by them is one of the most important environmental problems[3, 4]. There are many sources of heavy metals in agricultural soils, such as fertilizers, irrigation water, atmospheric deposition, soil-forming matrices, and river substrates[5]. The factors affecting soil heavy metal content are generally classified into two categories: natural and anthropogenic factors. Natural factors

mainly refer to soil-forming matrix; anthropogenic factors are mainly human activities, such as urban life, industrial production, agricultural production, transportation, etc. According to the survey of the Ministry of Agriculture, the annual food production polluted by heavy metals and reduced by heavy metal pollution is up to more than 22 million tons[6-8].

The study of river sediments has received increasing attention in recent years. The adsorption of heavy metals by bottom sediments forms hidden pollution[9], which is transformed into stable pollutants under the influence of external factors. Studies have shown that the historical pollution of rivers can be judged based on the pollution status of river substrates[10, 11]. The pollution of heavy metals in river bottom mud will not only pollute the river water, but also affect the surrounding agricultural soil through irrigation[12], which will pollute the agricultural soil. River sediment is an organic part of the earth's surface ecological and geological environmental system and an important material host in the water body environment[11, 13]. Once a river is polluted, pollutants that are not easily degradable, etc. are deposited in the bottom mud by adsorption or precipitation, and heavy metals are difficult to remove through natural migration transformation processes compared to nitrogen and phosphorus nutrients and organic pollutants[14, 15].

In this study, the bottom sediment of Jianggou River and its tributaries and the surrounding farmland soil were used as the research objects. The pollution characteristics and spatial distribution characteristics of eight heavy metal elements, Cr, Hg, As, Cu, Zn, Ni, Pb and Cd in farmland soil were analyzed and the correlation analysis of heavy metal contents in farmland soil and bottom sediment was conducted. It is expected to provide a basis for further development of ecological protection and heavy metal pollution prevention and control in the area, and to provide a reference for rational use and scientific management of farmland.

2. Materials and Methods

2.1 Overview of the Study Area

Jiaozuo is located in the northwestern part of Henan Province, south of the Taihang Mountains, a mid-latitude region with a warm-temperate continental monsoon climate, with an average annual temperature at 15.2°C and an average annual precipitation of 572.3 mm. Jiaozuo has two main water systems, the Yellow River and the Hai River. Among them, the study area is Tributary 1 and Tributary 2. Tributary 1 and Tributary 2 intersect in Wuzhi County and then flow into Jianggou River and then into Dasha River.

Tributary 1 and Tributary 2 originate in Boai County, Jiaozuo City, and Tributary 1 flows through Qinghua Township and Jincheng Township in Boai County into Xiaodong Township in Wuzhi County and reaches the study area through Daicun. Tributary 2 is the largest drainage channel in Boai County, flowing through several towns and administrative villages, with a total length of 25.12 km in Boai, and flows through Wuzhi County before joining the Jianggou River. The two tributaries receive domestic sewage from the urban areas of Boai County and the rural areas along the river, and the industrial wastewater from the coastal enterprises was discharged into the two tributaries in the historical period, but in recent years, the sewage has been treated centrally and the impact of domestic sewage on the two tributaries has been reduced compared to previous years. However, due to the cumulative nature of heavy metals, etc., the excessive discharge of sewage in the historical period led to the accumulation of heavy metals in the river bottom mud, which in turn polluted the surrounding farmland soil through river irrigation.

2.2 Sample Collection and Analysis

Soil sampling points of agricultural fields collected 0-20cm surface layer, each sampling point selected a square sampling area of 1 m², using a wooden shovel to take the four apexes of the square and the center of the soil mixed well, each soil sample to take about 1kg; in the tributary 1 and tributary 2 of the upper middle and lower reaches and the Jianggou River, respectively, in the closer to the river soil sampling, a total of 18 soil samples, number N1-N18 At the river sediment sampling

point, we took about 1kg of mixed sediment samples from both sides of the river section and the middle line of the river, put them into wide-mouth bottles and sent them back to the laboratory for testing in a holding tank. A total of 12 river sediment monitoring samples were set up on the river, numbered 1-12 (Figure 1). The soil and sediment samples were brought back to the laboratory, removed from plant roots and stones, etc., dried and ground naturally at room temperature, passed through 60 and 100 mesh nylon sieves (to ensure that the samples were sufficiently dry), and stored in labeled sample bags in preparation for the next step of disintegration.

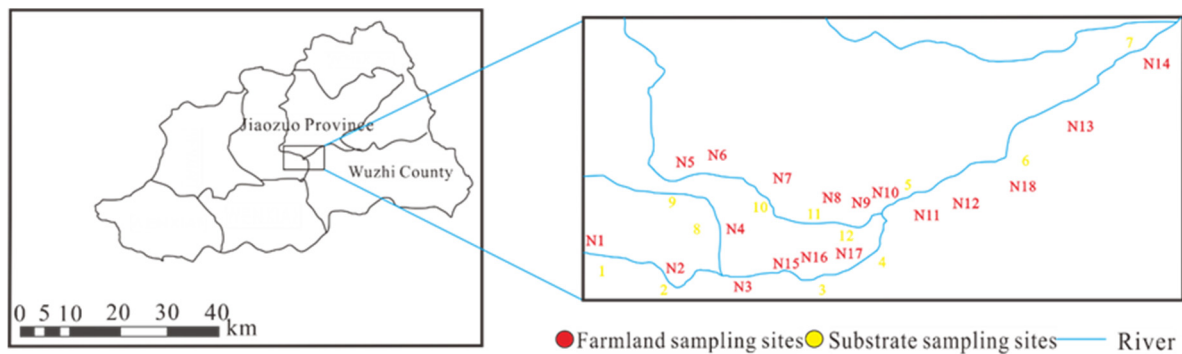


Figure 1. Location of Jianggou River Basin and distribution of sampling points

Take 0.20 g of the sample after pretreatment, put it into the digestion tank and add a small amount of deionized water. Add 6 ml of nitric acid, 2 ml of hydrofluoric acid and 2 ml of hydrogen peroxide in order to mix them well. Pay attention to the correct use of temperature and pressure sensors during the experiment. Put the digestion tank on the stand and then slowly put it into the microwave digestion device. Wait for it to cool to room temperature before slowly removing it. The process of pressure relief and deflation should be done in a fume hood with safety precautions and the whole operation should be slow. The process of driving acid should be done by placing the digestion tank on the stand and cooling the tank to room temperature when the solution becomes viscous. Some residual liquid can be rinsed with nitric acid to remove the residue by using the residual temperature, and finally transferred to a volumetric flask, fixed and mixed well, and then used for determination after clarification.

2.3 Heavy Metal Pollution Evaluation Methods

2.3.1 Single Factor Pollution Index Method

The single factor pollution index method evaluates the degree of pollution of a pollutant in the soil. Its calculation formula is.

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

In equation 1, P_i is the single pollution index of a heavy metal, C_i is the actual measured value of the heavy metal, and S_i is the soil screening value, and the soil screening value in the soil environmental quality control standard for soil pollution on agricultural land (GB15618-2018) is used as the reference value for pollution evaluation. The contamination level and pollution status can be determined according to the mean value of P_i , as shown in Table 1.

2.3.2 Nemero Integrated Pollution Index Method

The calculation formula is:

$$P_{synthesis} = \sqrt{\frac{P_1^2 + P_2^2}{2}} \quad (2)$$

In equation 2, P_1 is the maximum pollution index of a single pollutant, and P_2 is the average value of the index of each pollutant in the soil.

Soil heavy metal pollution was classified into five classes based on the single factor pollution index method and the Nemero integrated pollution index method, as shown in Table 1.

Table 1. Soil heavy metal pollution evaluation grading standards

| Pollution grade | Single factor pollution index | | Combined pollution index | |
|-----------------|-------------------------------|-------------------|--------------------------------|-------------------|
| | Mean Value Range | Grade Description | Range of values | Grade Description |
| I | $P_i \leq 0.7$ | Cleanliness | $P_{synthesis} \leq 0.7$ | Security |
| II | $0.7 < P_i \leq 1$ | Shang Cleaning | $0.7 < P_{synthesis} \leq 1.0$ | Alert level |
| III | $1 < P_i \leq 2$ | Light pollution | $1.0 < P_{synthesis} \leq 2.0$ | Light pollution |
| IV | $2 < P_i \leq 3$ | Medium pollution | $2.0 < P_{synthesis} \leq 3.0$ | Medium pollution |
| V | $P_i > 3$ | Heavy pollution | $P_{synthesis} > 3.0$ | Heavy pollution |

2.3.3 Potential Ecological Risk Index Method

The potential ecological risk index method is a method of soil heavy metal pollution evaluation developed from the sedimentological direction [16]. It is mainly based on the characteristics of the nature and environmental behavior of heavy metals. The ecological and environmental effects of heavy metals are linked to the toxicology while considering the soil heavy metal content. Its calculation formula is.

$$C = \frac{C_1}{C_2} \quad E = T \times C \quad RI = \sum_{i=1}^n E \quad (3)$$

C in Equation 3 is the contamination factor for a particular heavy metal. C_1 is the actual measured content. C_2 is the reference value (taken from the soil screening value). E is the potential ecological hazard factor, and the degree of risk is judged according to its mean value range.

T is the toxicity response factor (Cd: 30, As: 10, Pb: 5, Cr: 2, Cu: 5, Hg: 40, Ni: 5, Zn: 1), RI is the combined potential ecological hazard index of multiple heavy metals, and the ecological risk classes are classified as shown in Table 2.

Table 2. Classification standard of potential ecological hazards of heavy metals

| Single-factor potential ecological hazard factor | | Comprehensive potential ecological hazard index | |
|--|----------------------------------|---|-----------------------------|
| Mean Value Range | Risk level | Range of values | Risk level |
| $E < 40$ | Minor ecological risk | $RI < 150$ | Minor ecological risk |
| $40 \leq E < 80$ | Medium ecological risk | $150 \leq RI < 300$ | Medium ecological risk |
| $80 \leq E < 160$ | Sino-strong ecological risk | $300 \leq RI < 600$ | Sino-strong ecological risk |
| $160 \leq E < 320$ | Strong ecological risk | $RI \geq 600$ | Strong ecological risk |
| $E \geq 320$ | Extremely strong ecological risk | | |

2.4 Data Analysis

The data were analyzed by SPSS18.0 statistical software for correlation coefficients, and ArcGIS was used to characterize the soil heavy metal content and spatial distribution in the study area.

3. Results and Discussion

3.1 Characterization of Heavy Metal Pollution in Agricultural Soils

The statistical results of the content of eight heavy metal elements in the agricultural soils of the study area are shown in Table 3. As can be seen from Table 3, the average contents of heavy metal elements (Cd, Cr, As, Pb, Hg, Zn, Cu and Ni) in eight agricultural soils were 1.49, 73.32, 10.76, 39.99, 0.05, 63.91, 62.15 and 43.17 mg/kg, respectively. Compared with the background values of soil environment in Henan Province, except for Hg, the average contents of soil heavy metals such as Cd, Cr, As, Pb, Zn, Cu and Ni were higher than the background values of Henan soil, which were 9.93, 1.08, 1.08, 0.23, 1.04, 2.83 and 1.56 times of the background values, and the proportion of samples with Cd, Cu and Ni exceeding the background values were 100%, 94% and 83%, respectively. This indicates that there is an overall high degree of accumulation of the three heavy metals in the agricultural soils of the study area. Chunfang Li et al[17] found that the mean value of heavy metals Cd in farmland soils in the sewage irrigation area of Longkou was 3.06 times higher than the local background value, and the enrichment was the most obvious and mainly influenced by anthropogenic factors, with sewage irrigation being the main co-polluting factor.

The analysis of soil heavy metal content in the study area under the corresponding pH conditions compared with the risk screening values of GB15618-2018 revealed that the pH of the farmland in the area was greater than 7.5, and only Cd and As had exceeded the standard samples compared with the risk screening values of soil contamination on agricultural land, with the largest exceedance rate of 78.7% for Cd and 5% for As.

The coefficient of variation (CV) reflects the average degree of variation of heavy metal content in the overall sample, and the larger the coefficient of variation, the greater the influence of anthropogenic disturbances on heavy metals[18]. The degree of variation of heavy metals in agricultural soils in the study area was Pb>As>Cu>Ni>Cr>Zn>Hg>Cd in order, and the coefficients of variation of Pb and As in agricultural soils were the largest, 72.0% and 50.0%, indicating that Pb and As in soils were mainly contaminated by point sources. The coefficients of variation of Cu, Ni, Cr, Zn, Hg, and Cd were smaller, indicating that the above six heavy metals in the vicinity of the two tributaries were The degree of contamination of the above six heavy metals in agricultural soils near the two tributaries is relatively light and evenly distributed in space, which is less affected by human activities.

Table 3. The heavy metal content of farmland soil in the study area

| Element | Cd | Cr | As | Pb | Hg | Zn | Cu | Ni |
|---------------------------------|------|--------|-------|--------|------|-------|-------|-------|
| Min(mg/kg) | 0.28 | 44.65 | 5.60 | 19.59 | 0.03 | 45.34 | 21.49 | 22.06 |
| Max(mg/kg) | 4.98 | 128.91 | 25.69 | 120.67 | 0.07 | 91.20 | 96.95 | 67.54 |
| Average value(mg/kg) | 1.49 | 73.32 | 10.76 | 39.99 | 0.05 | 63.91 | 62.15 | 43.17 |
| Coefficient of variation(mg/kg) | 0.19 | 0.32 | 0.50 | 0.72 | 0.22 | 0.22 | 0.38 | 0.36 |
| background values(mg/kg) | 0.15 | 67.60 | 10.00 | 23.60 | 0.22 | 61.50 | 22.0 | 27.60 |
| screening value(mg/kg) | 0.6 | 250 | 25 | 170 | 3.4 | 300 | 100 | 190 |
| control value(mg/kg) | 4.0 | 1300 | 100 | 1000 | 6.0 | / | / | / |

3.2 Spatial Distribution Characteristics of Heavy Metals in Agricultural Soils

Based on the Arcgis inverse distance weighted interpolation method, the spatial distribution of heavy metals in agricultural soils around rivers in the study area was analyzed. The spatial distribution of eight heavy metals in the region, there is some variability and similarity.

As can be seen from Figure 2, the areas where the Cd and As contents exceed the soil control values are mainly located near the confluence of Tributary 1 and Tributary 2, with the highest Cd contents

of 4.66 mg/kg and 4.98 mg/kg at sampling points N9 and N17, respectively, and the As content of 25.69 mg/kg at sampling point N17; the Cd and As in agricultural soils at the confluence of Tributary 1 and Tributary 2 are of concern . By the study of heavy metal enrichment characteristics and pollution evaluation of Tuo River in Suizhou City, Su Haimin et al[19] found that Cd and As under sewage irrigation at the confluence of rivers had a greater impact on the surrounding farmland. high values of Cr content were mainly distributed in the upstream of tributary 1 and near the confluence of tributary 1 and tributary 2, and the farmland sites with the highest value of content distribution N9 were also far from the road.

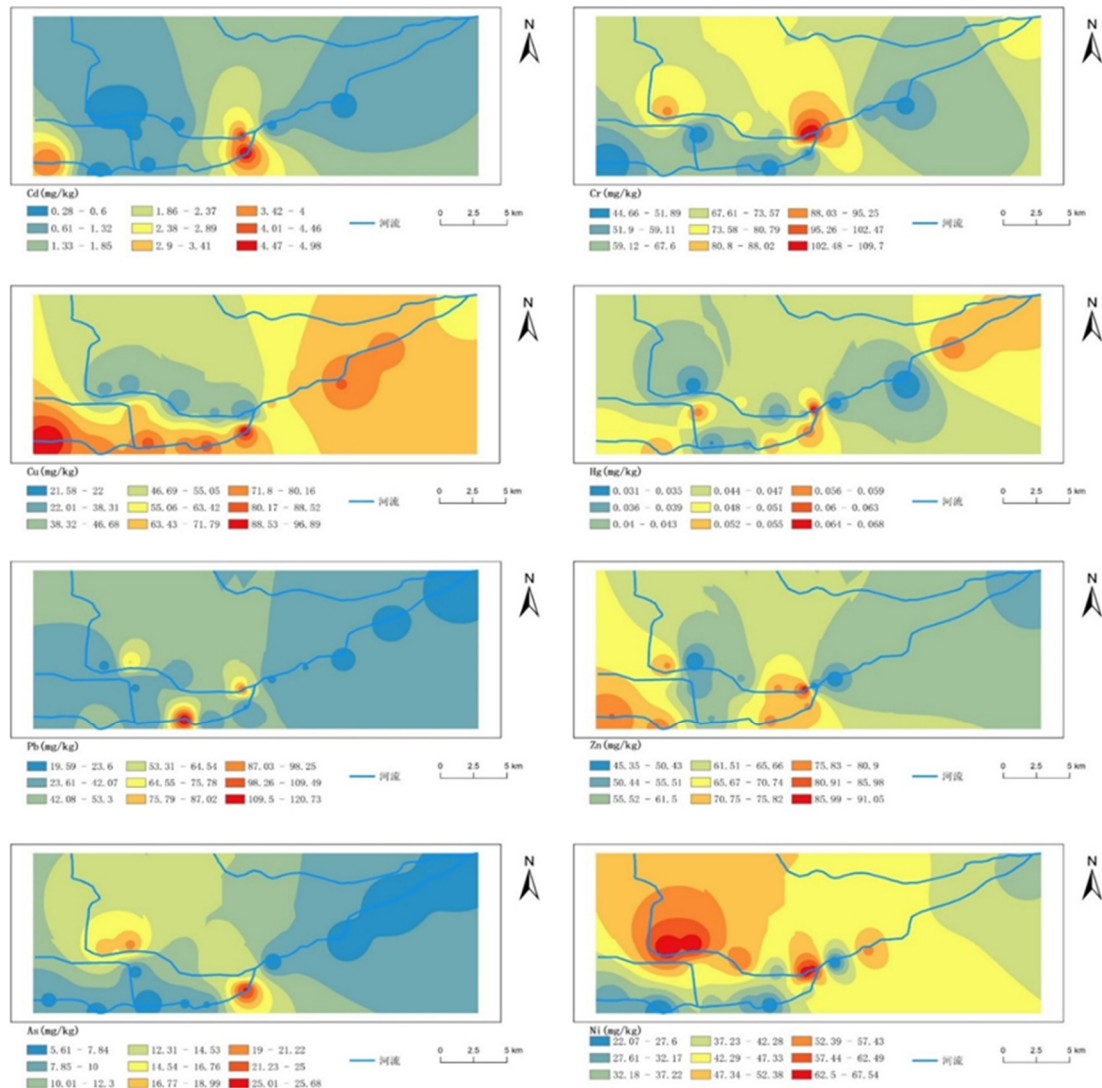


Figure 2. Spatial distribution of content in farmland soil in the study area

The spatial distribution of Cu and Ni differed greatly near Tributary 1 and Tributary 2; the Cu content in the south of the river was significantly higher than that in the north, and the high values were mainly concentrated in the middle and upper reaches of the river and Tributary 2; the Ni content in the north and southeast of the river was significantly higher than that in the southwest, and the high values were mainly concentrated in the downstream of Tributary 1 and the confluence of Tributary 1 and Tributary 2 in the north of the basin. The spatial distribution of Pb in the watershed is relatively uniform, with high values concentrated in the middle of Tributary 2 and the maximum content occurring in the N15 farmland sampling site. Yang Yu et al[20] found that the spatial distribution of six heavy metals in arable soils in the sub-basin was enriched at the mining activity area and its downstream and at the township streets in the western part of the sub-basin, and some high values of

heavy metals existed on both sides of the main river channel in the basin, indicating that the most important sources of pollution in the study area were mining and metallurgical activities and irrigation with polluted river water. The high value of Zn content is distributed in the confluence of tributary 1 and tributary 2 and the farmland near the downstream, and the Zn content of N10 farmland is 91.20 mg/kg.

3.3 Evaluation Analysis of Heavy Metal Pollution in Agricultural Soils

According to the evaluation criteria of P_i and $P_{synthesis}$ the proportion of different pollution levels of soil heavy metals in agricultural soil sampling points around the polluted rivers was analyzed, as shown in Table 4, through the single factor pollution index to see P_i can be seen that the pollution level of eight heavy metal elements are $Cd > Cu > As > Cr > Pb > Ni > Zn > Hg$, in which the pollution levels of Cu, As, Cr, Pb, Ni, Zn, and Hg in agricultural soil are I, which are all clean levels. The average pollution index of Cd is 2.49, and the pollution level is medium pollution, and the heavily polluted sample points account for 33.33% of the total sample points, which indicates that the pollution level of Cd in agricultural soils in the study area is high. The average pollution index of element As is less than 1, but the pollution index of some sampling points is 1.05, and there is an excess phenomenon, which should also attract attention. From the comprehensive pollution index $P_{summary}$, it can be seen that some of the farmland soil sample points in the watershed have exceeded the alert value, and the overall situation of light pollution, including light pollution, moderate pollution, and heavy pollution sample points are 16.67%, indicating that the Jianggou River and its two tributaries farmland soil by a certain degree of heavy metal pollution, need to pay attention to in future agricultural production.

Table 4. Single factor pollution index and comprehensive pollution index of heavy metals in farmland soil

| Statistical quantities | Cd | As | Pb | Cr | Zn | Ni | Cu | Hg | Combined pollution index |
|------------------------|------|------|------|------|------|------|------|------|--------------------------|
| Maximum value | 8.3 | 1.03 | 0.71 | 0.44 | 0.3 | 0.36 | 0.97 | 0.02 | 5.94 |
| Minimum value | 0.47 | 0.22 | 0.12 | 0.18 | 0.15 | 0.12 | 0.21 | 0.01 | 0.51 |
| Average value | 2.49 | 0.43 | 0.24 | 0.27 | 0.21 | 0.23 | 0.62 | 0.01 | 1.88 |

Table 5. Potential pollution index of heavy metals in farmland in the study area

| Statistical quantities | Cd | As | Pb | Cr | Zn | Ni | Cu | Hg | RI |
|------------------------|----------|-------|-------|-------|-------|-------|-------|-------|--------|
| Maximum value | 249 | 10.3 | 3.55 | 0.88 | 0.3 | 1.8 | 4.85 | 0.8 | 267.31 |
| Minimum value | 14.1 | 2.2 | 0.6 | 0.36 | 0.15 | 0.6 | 1.05 | 0.4 | 23.50 |
| Average value | 74.73 | 4.31 | 1.2 | 0.54 | 0.21 | 1.14 | 3.11 | 0.56 | 85.79 |
| Risk level | Moderate | Minor | Minor | Minor | Minor | Minor | Minor | Minor | Minor |
| Minor | 50 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | |
| Moderate | 17 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| Medium Strength | 17 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| Strong | 16 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| Extremely strong | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |

The results of the calculation of potential ecological risk coefficient and potential ecological risk index and their proportion in the study area are shown in Table 5: the mean values of the ecological hazard index of heavy metals in agricultural soils in the study area from high to low are: $Cd > As > Cu > Pb > Ni > Cr > Hg > Zn$; only the mean value of the potential ecological risk coefficient of Cd exceeds 40, which is 74.73, and the mean values of As, Cu, Pb, Ni, Cr, Hg and Zn The average value is less than 40; the average value of potential ecological risk index RI of eight heavy metal

elements in the study area is 85.79, which is a slight risk level. From the proportion of ecological risk coefficients, it can be seen that 16% of the sampling sites Cd reached a very strong ecological risk level, 17% of the sampling sites Cd reached a strong ecological risk level, and 17% of the sampling sites Cd reached a medium ecological risk level. According to the calculation results of potential ecological hazard contribution rate, it is concluded that the potential ecological risk contribution rate of Cd in the study area reaches 87%, and the contribution rate of Cr, Hg, As, Cu, Zn, Ni and Pb accounts for 13%, Cd is the main pollution factor and should be focused on.

3.4 Characteristics of Heavy Metal Content in River Sediments

The results of heavy metal content analysis of river sediment in the study area can be learned from Table 6, the average contents of eight heavy metal elements (Cd, Cr, As, Pb, Hg, Zn, Cu and Ni) were 10.80, 57.79, 21.38, 20.11, 0.21, 108.61, 45.53 and 39.03 mg·kg⁻¹, which were compared with the background values of soil environment in Henan Province. Compared with the background values, Cd, Cr, As, Pb, Hg, Zn, Cu and Ni in the substrate had sampling points that exceeded the background values; the average contents were 72, 0.85, 2.14, 0.85, 0.95, 1.77, 2.07 and 1.41 times of the background values; the percentages of samples with Cd, As, Zn and Ni exceeding the background values were 100%, 96%, 87% and 74%, respectively. 87% and 74%, respectively, indicating that there is an overall high degree of accumulation of the above four heavy metals in the bottom sediment. Compared with the soil screening value, the exceedance rates of Cd, As and Cu in the bottom sediment were 100%, 26% and 4%, and the maximum exceedance times were 62.8 times, 1.96 times and 1.03 times respectively, while the other elements did not exceed the soil screening value standard, in addition, 39% of the samples of Cd exceeded the soil control value; therefore, the river should strengthen the management when dredging and should not be returned to the field directly.

From the viewpoint of the coefficient of variation, the degree of variation of heavy metals is Pb>As>Cu>Ni>Cr>Zn>Hg>Cd, and the coefficients of variation of Cd, As and Hg heavy metals in the sediment of the study area are over 60%, especially the coefficients of variation of Cd and Hg are as high as 113% and 120%, and the pollution distribution is uneven and seriously disturbed by human social behavior; the coefficients of variation of Pb, Cu, Ni, Cr and The coefficients of variation of Pb, Cu, Ni, Cr and Zn are weakly divergent at 0.3-0.6, with low dispersion and relatively uniform pollution distribution, and less influenced by human activities. From the results, the enrichment factors of As, Cu, Zn, Ni and Cd were all greater than 1, and the average contents exceeded the soil background values, indicating that As, Cu, Zn, Ni and Cd were enriched in the sediment; the enrichment factor of Cd reached 72.00, and Cd in the sediment showed a strong enrichment effect. The enrichment factors of Cr, Pb and Hg in the sediment were less than 1, and the mean values did not exceed the soil background values, indicating that Cr, Pb and Hg were more stable in the sediment of the rivers in the study area.

Table 6. Heavy metal content in the mud at the bottom of the river

| | Cd | Cr | As | Pb | Hg | Zn | Cu | Ni |
|---------------------------------|-------|--------|-------|-------|------|--------|--------|-------|
| Min(mg/kg) | 0.79 | 28.55 | 9.10 | 5.53 | 0.04 | 22.27 | 14.80 | 16.90 |
| Max(mg/kg) | 37.69 | 180.40 | 48.97 | 35.43 | 1.01 | 173.97 | 103.12 | 80.79 |
| Average value(mg/kg) | 10.80 | 57.79 | 21.38 | 20.11 | 0.21 | 108.61 | 45.53 | 39.03 |
| Coefficient of variation(mg/kg) | 1.13 | 0.59 | 0.61 | 0.35 | 1.20 | 0.36 | 0.50 | 0.47 |
| Enrichment factors(mg/kg) | 72.00 | 0.85 | 2.14 | 0.85 | 0.95 | 1.77 | 2.07 | 1.41 |
| Background value(mg/kg) | 0.15 | 67.60 | 10.00 | 23.60 | 0.22 | 61.50 | 22.0 | 27.60 |
| Scale | 100% | 8% | 96% | 22% | 22% | 87% | 64% | 74% |
| Screening Value(mg/kg) | 0.6 | 250 | 25 | 170 | 3.4 | 300 | 100 | 190 |
| Control value(mg/kg) | 4.0 | 1300 | 100 | 1000 | 6.0 | /0 | / | / |

3.5 Correlation Analysis of Agricultural Soils and River Sediments

The correlation analysis of heavy metals in the polluted rivers and surrounding farmland soils were conducted separately, and the results are shown in the following table. The results from Table 7 show that Cd and As of agricultural soils in the study area are significantly correlated at the 0.01 level with a correlation coefficient of 0.673, indicating that Cd and As are homologous, and the correlation between Zn and Cu is significantly correlated at the 0.05 level with a correlation coefficient of 0.533. Wang Zhongyang [21] found that Cd and As are highly homologous after source analysis of heavy metals in Chaoyang District soils, and the source of pollution from a factory upstream of the river, which has a history of excessive effluent discharge. In addition, the correlation coefficients between Cd and Ni, Cu and As, Cr and Ni, Hg and Zn, and Pb were between 0.3 and 0.5, which were low correlations, while the correlation coefficients between other heavy metal elements were less than 0.3, which were not correlated. Therefore, Cd and As are the most likely to be influenced by the same exogenous source.

Table 7. Correlation between heavy metals in farmland soil around the study area

| Heavy Metals | Cd | As | Ni | Zn | Cr | Cu | Hg | Pb |
|--------------|---------|--------|--------|--------|--------|--------|--------|----|
| Cd | 1 | | | | | | | |
| As | 0.673** | 1 | | | | | | |
| Ni | -0.407 | 0.233 | 1 | | | | | |
| Zn | 0.063 | 0.249 | -0.292 | 1 | | | | |
| Cr | -0.100 | 0.262 | 0.435 | -0.119 | 1 | | | |
| Cu | -0.053 | -0.451 | -0.262 | 0.533* | 0.212 | 1 | | |
| Hg | 0.027 | -0.013 | -0.296 | 0.345 | 0.030 | 0.267 | 1 | |
| Pb | -0.232 | 0.253 | 0.212 | 0.030 | -0.079 | -0.234 | -0.426 | 1 |

Note: *. At the 0.05 level (two-tailed), the correlation is significant; **. At the 0.01 level (two-tailed), the correlation is significant

As can be seen from the previous paper, Cd and As in agricultural soils and river sediments in the study area have sampling points that exceed the soil screening values, and Cd and As are the elements of key concern. In order to investigate the relationship between soil heavy metal pollution and rivers in the study area, correlation analysis of these two heavy metal elements in farmland and river sediment was conducted in this paper. The correlation coefficient was 0.93, indicating that the Cd elements in farmland soils and river sediments were homologous; the As elements in farmland soils and river sediments were highly correlated. The correlation coefficient was 0.90, indicating that the Cd elements in agricultural soils and river sediments were also homologous. Combined with the previous investigation and the previous conclusion, it can be seen that Cd and As in river sediment and farmland soil are homologous. After investigation, in the 1980s and 1990s, there were more small and medium-sized battery, small smelting and small tannery enterprises in the study area, and coupled with the rough environmental management at that time, the sewage discharged by the enterprises might contain Cd and As. With the increase of environmental management in China, most of the small enterprises that did not meet the environmental protection requirements have been shut down, and the phenomenon of excessive sewage discharge has basically ceased to exist, but historically the use of Cd and As contaminated However, historically, the use of Cd and As polluted river water to irrigate farmland will have a certain impact on the content of Cd and As in the farmland soil around

the river, and the Cd and As deposited by the river bottom mud will also be brought to the farmland soil with the process of irrigation or river dredging.

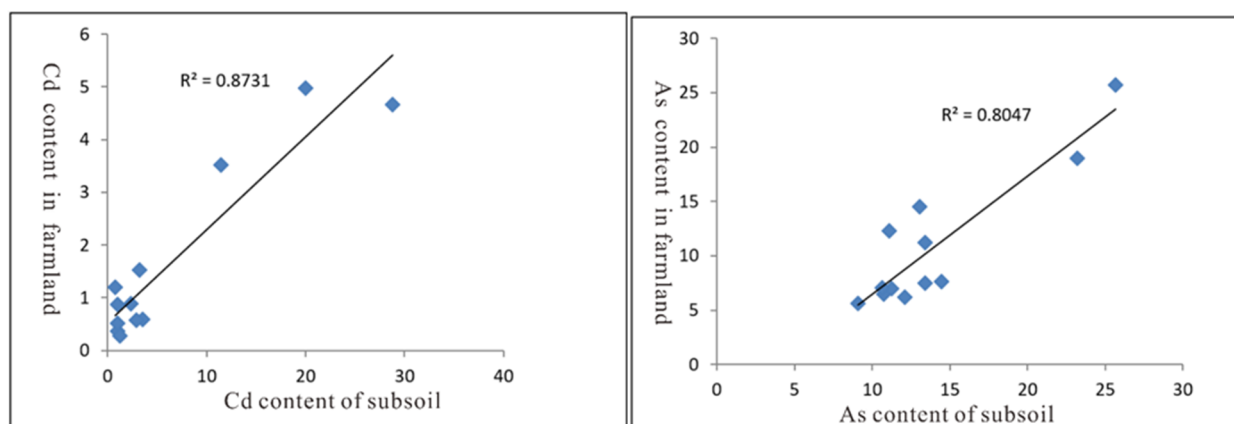


Figure 3. The correlation between farmland soil and river bottom mud heavy metals

4. Conclusion

- (1) The average values of heavy metals in agricultural soils in the study area, except for Hg, are higher than the background values of soils in Henan Province, and Cd, Cu and Ni have a significant cumulative effect; compared with the screening values of soil pollution risk in agricultural land, only the average contents of Cd and as elements exceed the standard. Among them, only individual farmland samples had extreme values of Hg, and the rest performed well; Hg is an exogenous pollutant.
- (2) The analysis results of single factor index method and Nemero integrated pollution index method show that Cd is the main pollution factor in the agricultural soil of the study area, with a strong risk of Cd pollution, and heavy metal pollution reaches light pollution level. The comprehensive potential hazard risk index RI shows that Cd reaches the medium ecological risk level and should be focused on.
- (3) The study area river sediment heavy metals except Cr and Pb, the average value of all other heavy metals content is higher than the background value of Henan soil, and Cd, As, Zn and Ni cumulative effect is significant; compared with the soil pollution risk screening value, all sample points of heavy metal Cd exceeded the standard, and the high degree of variability pollution distribution is not uniform, seriously disturbed by human social behavior. 26% exceeded the standard of As, only The exceedance rate of As was 26%, and only some sample points exceeded the standard.
- (4) The correlation analysis results show that the sources of Cd and As are similar. From the analysis, it can be seen that they mainly come from the irrigation of the surrounding rivers and the application of phosphorus fertilizer, and are highly correlated with Cd and As in the river sediment, and Cd, Cu, As and Ni in the agricultural soil are correlated with the river sediment.

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