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Heavy Metal Pollution Status and Potential Ecological Risk Assessment in Farmland Surface Soil Along River in Jiaozuo Area

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ABSTRACT

A total of 41 surface soil samples were collected from the farmlands along Guangliji River and Jianggou River in Jiaozuo area, and 7 heavy metals such As Cr, Cu, Zn, AS, Cd, Pb and Ni were determined by ICP-MS (Varian-820).The soil accumulation index method, single factor pollution index method, Nemerow comprehensive pollution index method and potential ecological risk index method were used to evaluate the pollution status and potential ecological risk of heavy metals in the study area. The results showed that compared with the risk screening value (pH>7.5) given in the "Soil Quality Standard for Soil Pollution Risk Control of Agricultural Land" (GB15618-2018), Cd in farmland soil along the two rivers exceeded the screening value by 5.7 times and 1.5 times, respectively, and was the main local pollutant. The Nemero comprehensive pollution index of the farmland along Guangliji River and Jianggou River was 9.71 and 1.88, respectively, which were in the level of heavy pollution and light pollution. The comprehensive potential ecological risk index of farmland along the two rivers is 417.65 and 85.79, with strong ecological risk and slight ecological risk respectively. The comprehensive evaluation shows that there is a certain degree of heavy metal pollution in the farmland soil along the river in Jiaozuo area, especially Cd pollution, and the ecological risk in some areas has exceeded the acceptable level, which should arouse the attention of the local government and relevant departments.

KEYWORDS

Heavy metal; Farmland soil; Earth accumulation index method; Pollution index method; Ecological risk assessment.

1. INTRODUCTION

In recent years, with the accelerating process of urban life and industrial and agricultural development, the unreasonable application of urban solid waste, industrial wastes, pesticides and fertilizers has worsened the soil pollution problem, especially the heavy metal pollution problem, resulting in the degradation of soil quality and the decline of agricultural production and quality[1, 2]. Heavy metals are highly toxic, harmful and not easily decomposed by microorganisms. Heavy metals in agricultural products can be enriched into human body through the food chain. Studies have shown that heavy metal pollution in farmland soil will cause serious harm to the ecosystem and human health[3-6]. China is a big agricultural country, farmland soil quality is an important factor to measure food security, and the protection of soil environmental quality is of great significance.

With the promotion of sewage irrigation technology, river surface water has become the main irrigation source of surrounding farmland soil, which solves the problem of irrigation water shortage, but also brings potential ecological risks to farmland soil[7, 8]. At present, the surface water quality in China has been greatly improved, and the content of heavy metals in surface water in Jiaozuo City does not exceed the standard. However, according to the previous research results and relevant data, the heavy metals in farmland soils around Guangliji River and Jianggou River exceed the standard[9-13]. Jiaozuo City is the core area of grain production in China, and the protection of soil environment is related to the safety of food and drinking water sources, the health of human settlements, and the construction of ecological civilization. Therefore, the study of heavy metal pollution in soil in this region and its risks is of great significance for local agricultural development and the protection of residents' health[14, 15]. In order to find out the pollution status of major rivers in Jiaozuo area, the pollution degree and potential ecological risk assessment of 7 heavy metals in farmland soil around Guangliji River and Jianggou River and their tributaries were discussed in this paper, which provided theoretical basis for further analysis of the sources of heavy metal pollution in farmland soil and reliable basic materials for rational use and scientific management of farmland.

2. MATERIALS AND METHODS

2.1. Sample collection and processing

According to the principle of "random" and "equal amount", 41 topsoil samples (0~20) were collected from the 3 km range of the north and south banks of the Guangliji River and the upper, middle and lower reaches of the Jianggou River and its two tributaries in areas far away from the main traffic lines, industrial zones and residential areas where human non-agricultural activities had a great impact on the farmland soil environment.The soil sample of about 1kg was stored by the "quarter method" and put into a self-sealing bag to mark the sampling information.The samples were air-dried, ground and put into polyethylene ziplink bags through 60 mesh and 100 mesh nylon screens for later experiments.

2.2. Determination of heavy metals in soil

0.20g (accurate to 0.0002g) of air-dried and sieved (100 mesh nylon sieve) samples were placed in Teflon digestion tank, followed by 6mL nitric acid, 2mL hydrofluoric acid and 2mL hydrogen peroxide, and then digested with microwave digester. After digestion, the digestion solution turned into a thick shape. After digestion and cooling, a small amount of nitric acid was added to rinse the digestion tank. After the residual temperature was used to dissolve and dissolve the inner wall residue of the tank, the digestion solution was moved to a 50mL volumetric bottle, the volume was fixed to the line, and the digestion solution was mixed well. After the fixed volume was passed through the 0.45μm filter membrane, 7 heavy metals such As Cr, Cu, Zn, AS, Cd, Pb and Ni were determined by ICP-MS (Varian-820).

2.3. Evaluation method

2.3.1. Earth accumulation index method

The earth accumulation index method was proposed by Muller in 1969 [16].The method for quantitative evaluation of the degree of accumulation of heavy metals relative to historical background values or the degree of influence by human factors is calculated as follows:

$$Igeo=\log_2 \frac{C_n^i}{KC_s^i}$$

Where: Igeo is the ground accumulation index of pollutant i in soil; C_n^i is the measured value of pollutant i; C_s^i is the background value of pollutant i (This paper selects the background value of soil heavy metal elements in Henan Province as the reference standard value [17, 18], K value is the coefficient that different soil types may cause changes in background value. In this study, K value is 1.5.

The evaluation and grading standards of land accumulation index are shown in Table 1.

Table 1. The evaluation and grading standard of the accumulation index

Igeo	Fractionation	Pollution degree
<0	0	Pollution-free
0~1	1	Light to moderate contamination
1~2	2	Moderate pollution
2~3	3	Moderate to strong contamination
3~4	4	Strong pollution
4~5	5	Strong to extremely severe pollution
>5	6	Extreme pollution

2.3.2. Single factor pollution index method

Single factor pollution index is an evaluation method to evaluate the pollution degree of a single factor in a specific area. It is expressed by the ratio of the actual pollution level to the standard limit value. The larger the value, the more serious the pollution is [19].

The formula for the single-factor pollution index is as follows:

$$P_i = \frac{C_i}{S_i}$$

P_i is the pollution index of heavy metal contaminant i in soil; C_i is the measured value of heavy metal pollutant element i, mg/kg; S_i is the evaluation standard value of heavy metal pollutant element i (this paper selects the risk screening value given in the "Soil Quality and Agricultural Land Soil Pollution Risk Control Standard" (GB15618-2018) pH>7.5 as the evaluation standard), mg/kg.

The grading standards are shown in Table 2.

Table 2. Single factor pollution index evaluation grading standards

Fractionation	P_i	Pollution degree
1	$P_i \leq 1$	Pollution-free
2	$1 < P_i \leq 2$	Light pollution
3	$2 < P_i \leq 3$	Moderate pollution
4	$P_i > 3$	Heavy pollution

2.3.3. Nemerow comprehensive pollution index method

Nemerow comprehensive pollution index method is a common method to evaluate heavy metal pollution status, reflecting the average pollution degree of various heavy metals on soil, highlighting the impact of high concentrations of heavy metals on soil environmental quality[20]. The formula for Nemerow's comprehensive pollution index is as follows:

$$PI = \sqrt{\frac{(P_{iave})^2 + (P_{imax})^2}{2}}$$

PI is the comprehensive pollution index of heavy metal elements in soil; P_{iave} is the average value of single factor pollution index of various heavy metal elements; P_{imax} is the maximum single factor pollution index in different kinds of heavy metal elements. The grading standards are shown in Table 3[21].

Table 3. Nemero comprehensive pollution index evaluation and grading standards

Fractionation	PI	Pollution degree
1	PI<0.7	Pollution-free
2	0.7< PI≤ 1	Warning line
3	1< PI≤2	Light pollution
4	2< PI≤3	Moderate pollution
5	PI >3	Heavy pollution

2.3.4. Potential ecological risk assessment method

The potential ecological risk index evaluation method was proposed by Hakanson, which comprehensively considered the content and toxicity characteristics of heavy metals in environmental media and was widely used to evaluate the degree of heavy metal pollution in environmental media[22-24]. Its calculation formula is as follows:

$$E_r^i = T_r^i \times P_i$$

$$RI = \sum_{i=1}^{n} \left(T_r^i \times P_i\right)$$

RI is the comprehensive potential ecological risk index of multiple heavy metals in soil; E_r^i is the single potential ecological risk factor of the i heavy metal. T_r^i indicates the toxicity factor of heavy metal i; The toxicity coefficients of different heavy metals are shown in Table 4[25]. P_i is the single factor pollution index of heavy metal i. Hakanson divides the single potential ecological risk coefficient and the comprehensive potential ecological risk coefficient into different levels, and the evaluation criteria for the potential ecological risk levels are shown in Table 5[26].

Table 4. Toxicity coefficients of different heavy metals

Types of heavy metals	Pb	Zn	Cd	Cr	Cu	As	Ni
T_r^i	5	1	30	2	5	10	5

Table 5. Hakanson potential ecological risk rating standards

E_r^i	RI	Ecological risk level
$E_r^i < 40$	RI < 150	Minor ecological risk
$40 \leq E_r^i < 80$	150 ≤ RI < 300	Medium ecological risk
$80 \leq E_r^i < 160$	300 ≤ RI < 600	Strong ecological risk
$160 \leq E_r^i < 320$	RI ≥ 600	Very Strong ecological risk
$E_r^i \geq 320$	—	Extreme ecological risk

3. RESULTS AND ANALYSIS

3.1. Characteristics of heavy metal content in farmland soils along rivers in Jiaozuo area

The test results of 7 heavy metals, including Pb, Zn, Cd, Cr, Cu, As and Ni, are shown in Table 6. As can be seen from the table, the average content of Pb, Zn, Cd, Cu and Ni5 heavy metals in the soil surface samples of farmland is significantly different in the surrounding areas of the two rivers. The content of Zn, Cu and NI5 heavy metals is higher in the farmland along the Guangliji River, while the content of Pb and Ni is higher in the farmland along the Jianggou River. The Cd content in the farmland soil around the river was higher than the background value of Henan Province soil, exceeding the standard rate by 100%. The average Cd content exceeded the screening value of agricultural land soil risk, and the Cd content in some farmland soil exceeded the control value of agricultural land soil pollution risk. Compared with the screening values, the excess rate of Cd and Cu in the soil around Guangliji River was 65.2%, 52.2%, 55.6% and 5.6% respectively.There is serious pollution of Cd in the farmland around the two rivers, and the pollution around Guangliji River is more serious than that around Jianggou River.

Table 6. Detection results of heavy metals in farmland soils around Guangliji River and Jianggou River (mg/kg)

Item	Pb	Zn	Cd	Cr	Cu	As	Ni
Kwangliji River (n=23) Mean value	26.36	163.32	4.02	74.97	118.85	15.14	28.90
Jianggou River (n=18) mean value	39.99	63.91	1.49	73.32	62.15	10.76	43.17
Soil background values	21.8	61.9	0.065	62.5	20	9.8	27.3
Screening value (pH > 7.5)	170	300	0.6	250	100	25	190
Control value	1000	—	4.0	1300	—	100	—

3.2. Pollution situation of farmland along river in Jiaozuo area

Using the soil background value of Henan Province as the basis, the average accumulation index of each heavy metal element was calculated, as shown in Table 7. All samples of Cd were contaminated; Cu and Zn samples with Igeo>0 accounted for 95.1% and 56.1% of the total samples, respectively. The number of Pb, As and Ni Igeo>0 samples was less than 50% of the total samples. Cr was the least contaminated sample, accounting for 14.6%. The average Igeo of Cd is 2.7, the classification is 3, and the pollution degree is medium to strong pollution. The maximum Igeo of Cd is 8.2, which has reached the extremely serious pollution degree in the farmland soil around Guangliji River. The average Igeo of Cu element in the farmland soil around Guangliji River was in the range of 1~2, indicating moderate pollution. The average Igeo of Zn element is between 0 and 1, which is mild pollution. The average Igeo of Cu element in the farmland soil around Jianggou River is in the range of 0~1, which belongs to light pollution. The average Igeo value of Zn element is within the range of classification 0, and it is in a pollution-free state. The average Igeo values of As, Ni and Cr are all less than 0, indicating no pollution in general, but slight pollution exists in individual sampling points. Figure 1 shows the histogram of ground accumulation index of 7 heavy metals in the farmland soil around the two rivers. It can be seen from the graph that Cd and Cu pollution are prevalent in the farmland surface soil around the rivers in Jiaozuo area, and Cd pollution is serious, while Zn and Pb are lightly polluted in some areas.

Table 7. Statistical table of soil accumulation index (Igeo) of heavy metals in farmland soils along rivers in Jiaozuo area

Item	Pb	Zn	Cd	Cr	Cu	As	Ni
Guanglij River(n=23)							
Mean value	-0.19	0.82	2.67	-0.38	1.87	-0.20	-0.49
Maximum value	0.64	1.36	8.20	0.29	2.69	0.24	0.19
Minimum value	-0.54	0.18	0.93	-0.93	0.90	-1.07	-0.92
>0 percent	17.4	100.0	100.0	0.08	100.0	21.7	0.04
>1 percent	0.0	21.7	95.7	0.0	95.7	0.0	0.0
Pollution level	Pollution -free	Light pollution	Moderate pollution	Pollutio n-free	Moderate pollution	Pollution -free	Pollution-free
Jianggou River(n=18)							
Mean value	0.18	-0.53	2.73	-0.47	0.91	-0.48	0.06
Maximum value	1.77	-0.02	4.47	0.35	1.55	0.78	0.71
Minimum value	-0.85	-1.02	0.32	-1.18	-0.62	-1.42	-0.91
>0 percent	44.4	0.0	100.0	22.2	88.9	27.8	33.3
>1 percent	16.7	0.0	83.3	0.0	66.7	0.0	0.0
Pollution level	Light pollution	Pollution -free	Moderate pollution	Pollutio n-free	Light pollution	Pollution -free	Light pollution

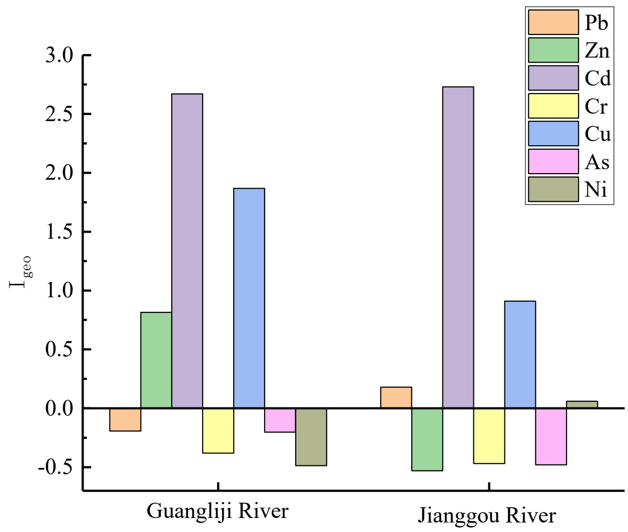

Figure 1. Soil accumulation index of 7 heavy metals in farmland soils around rivers in Jiaozuo

3.3. Evaluation of heavy metal pollution in farmland soil around rivers in Jiaozuo area Based

on the screening values in the "Soil Environmental Quality Standard for Soil Pollution Risk Control of Agricultural Land" (GB15618-2018) as the evaluation criteria, the single-factor pollution index method and Nemero comprehensive pollution index method were used to evaluate the soil heavy metal pollution in the farmland around Guanglji River and Jianggou River. The single factor pollution index of 7 heavy metals and the Nemero comprehensive pollution index were obtained, as shown in Table 8.

The average single-factor pollution index of Pb, Zn, Cr, As and Ni in the study area is between 0 and 1, and the pollution level is level 1, which is clean and pollution-free. However, the pollution index of As in some sampling points around Jianggou River is greater than 1, which is in the light pollution level. The average single-factor pollution index of Cd in the farmland soil surface of Guangliji River and Jianggou River were 13.4 and 2.49, respectively, and the pollution levels were severe pollution and moderate pollution, respectively. The soil Cd pollution in the farmland around Guangliji River was the most serious, and the maximum single-factor pollution index was 108.5.Cu was also slightly polluted in the soil around Guangliji River, and the single factor pollution index was 1.91.

According to Nemero's comprehensive pollution index, among the 41 samples, 10 sampling points had PI<0.7, accounting for 24.39% of the total samples, and were in the clean pollution-free level; 9 sampling points had 0.7 < PI < 1, accounting for 21.95% of the total samples, and were in the alert level, soil quality is still clean; 11 sampling points had 1 < PI < 2, accounting for 26.83% of the total samples, and were in the light pollution level; 3 sampling points had 2 < PI < 3, accounting for 7.32% of the total samples, and were in the moderate pollution level; 8 sampling points had PI > 3, accounting for 19.51% of the total samples, and were in the heavy pollution level.

Table 8. Heavy metal single factor pollution index and Nemero comprehensive pollution index

	Pb	Zn	Cd	Cr	Cu	As	Ni	PI
Guangliji River(n=23)								
Mean value	0.22	0.65	13.4	0.38	1.19	0.5	0.29	9.71
Maximum value	0.38	0.93	108.5	0.58	1.91	0.67	0.46	77.38
Minimum value	0.17	0.41	0.7	0.25	0.55	0.27	0.21	0.58
Pollution level	Pollution-free	Pollution-free	Heavy pollution	Pollution-free	Light pollution	Pollution-free	Pollution-free	Heavy pollution
Jianggou River(n=18)								
Mean value	0.24	0.21	2.49	0.27	0.62	0.43	0.23	1.88
Maximum value	0.71	0.30	8.30	0.44	0.97	1.03	0.36	5.94
Minimum value	0.12	0.15	0.47	0.18	0.21	0.22	0.12	0.51
Pollution level	Pollution-free	Pollution-free	Moderate pollution	Pollution-free	Pollution -free	Pollution-free	Pollution-free	Light pollution

3.4. Potential ecological risk assessment index of farmland soil around rivers in Jiaozuo area

The single potential ecological risk coefficient E_r^i and the comprehensive potential ecological risk index RI of 7 heavy metals are shown in Table 9. Pb, Zn, Cu, Cr, As, Ni, etc. in the farmland soils around the two rivers are at a slight ecological risk level, but the potential ecological risk level of Cd reaches medium or above, and some sampling sites of Guangliji River belong to a very strong ecological risk level. From the perspective of comprehensive potential ecological risk index, the average value of comprehensive potential ecological risk index of Guangliji River is 417.65, which belongs to the strong ecological risk level. The average value of comprehensive potential ecological risk index of Jianggou River is 85.79, which belongs to slight ecological risk level. Therefore, the potential ecological risk of Cd in the farmland soil around the two rivers is high, and the ecological environment risk in the area and its surrounding should be paid more attention.

Table 9. Evaluation results of potential ecological risk index of sampling points

Heavy metal element	Guangliji River			Jianggou River		
	Mean value	Maximum value	Minimum value	Mean value	Maximum value	Minimum value
Pb	1.10	1.90	0.80	1.20	3.55	0.60
Zn	0.65	0.90	0.40	0.21	0.30	0.15
Cd	401.96	3255.60	21.10	74.73	249.00	14.10
Cr	0.77	1.20	0.50	0.54	0.88	0.36
Cu	5.96	9.60	2.80	3.11	4.85	1.05
As	5.04	6.70	2.70	4.31	10.30	2.20
Ni	1.45	2.30	1.10	1.14	1.80	0.60
RI	417.65	3276.00	33.50	85.79	267.31	23.50

The proportion of potential ecological risk levels of heavy metals in farmland soils around the two rivers is shown in Figure 2. The proportion of Pb, Zn, Cu, Cr, As, Ni and other potential ecological risk levels in farmland soils around the two rivers is 0, indicating low ecological risk. The medium and above potential ecological risk levels of Cd accounted for 39% and 50%, respectively, among which 17% of Cd sampling sites around Guangliji River belonged to extremely high ecological risk. Most of the comprehensive potential ecological risks of heavy metals in the farmland soil around the two rivers are slight risks, and Cd is the main ecological risk factor. Special attention should be paid to the potential ecological risks of Cd.

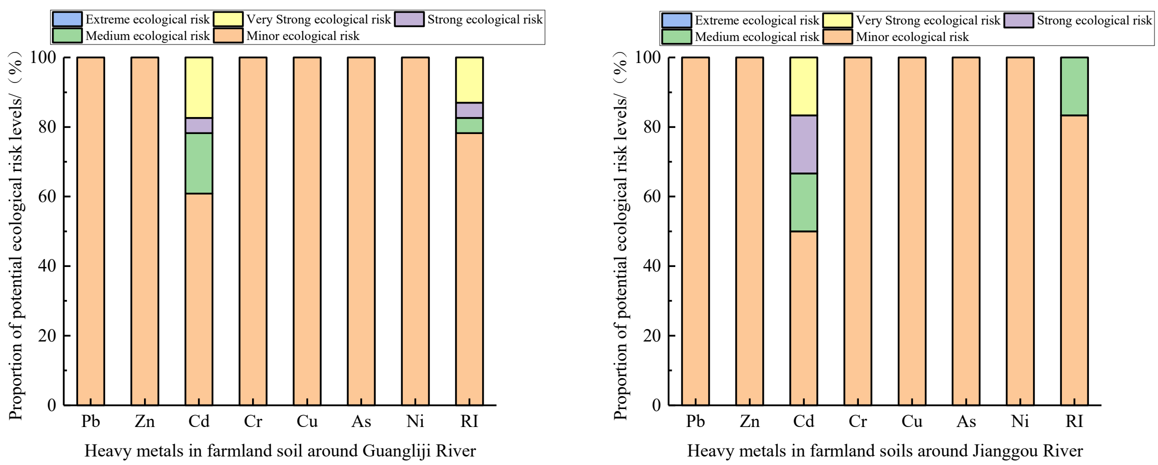

Figure 2. Proportion of potential ecological risk levels of heavy metals in farmland soils around rivers

4. DISCUSS

The results of this study showed that the agricultural soils along the Guangliji River and Jianggou River in Jiaozuo area were polluted by heavy metals to a certain extent, and 7 heavy metals such as lead, zinc, cadmium, chromium, copper, arsenic and nickel were all higher than the soil background value of Henan Province, among which the concentration of Cd was higher than the soil background value of Henan Province, and the exceeding rate was 100%. The maximum value of Cd in the surrounding farmland along Guangliji River and Jianggou River exceeded the soil environmental quality screening value by 107.52 times and 7.3 times, respectively, which belonged to severe pollution and moderate pollution. Xin Jiahui et al [27] studied the heavy metals in the soil of Jiaozuo City. The results showed that the average contents of Cr, Ni, Cu, Zn, As, Cd, Hg and Pb in the soil of agricultural area were 121.88, 44.78, 39, 74.83, 13, 42, 14 and 33.17mg/kg, respectively, and the main heavy metal polluting element was Cd. Zhang Jing et al[12] evaluated the degree of soil heavy metal pollution in Jiaozuo City, and the results showed that Cd, Pb and Hg were more harmful, and the Cd exceeded the standard rate was the highest, which was related to the mining industry and the local geological environment background. In the typical sewage irrigation area of Hebei Province, long-term sewage irrigation led to the accumulation of Cd in the soil surface to a certain extent[28]. There is serious heavy metal pollution in the sediment of Shihe River Basin in Jiyuan, among which Cd and Hg are the most serious pollution, and the farmland irrigated with sewage also has ecological risks[29]. Most industrial and mining enterprises in Jiaozuo City discharge industrial wastewater and waste residue into rivers, which become the main irrigation source of farmland soil around rivers, resulting in increasingly serious heavy metal pollution of farmland soil, and call on relevant departments to pay attention to protect food safety.

The ecological risk levels of heavy metals in farmlands along Guangliji River and Jianggou River are strong ecological risk and slight ecological risk, respectively, in which cadmium element has the highest ecological risk and zinc has the lowest ecological risk. Cd is the sixth toxic substance harmful to human health, with "carcinogenic, teratogenic and mutagenic" biological toxicity, excessive cadmium in soil will not only inhibit plant growth, but also accumulate in the human body through the role of the food chain, causing varying degrees of damage to human kidneys, bones, etc[30]. Some studies have analyzed that phosphate fertilizer and urea will increase the concentration of Cd in soil, and the improper application of chemical fertilizers and pesticides in agricultural production activities will also increase the pollution of heavy metals in farmland soil[31-33]. It is suggested that local residents should reduce the use of chemical fertilizers and pesticides, grow crops rationally, and relevant departments should control and improve farmland polluted by heavy metals, regularly test farmland soil environmental quality, and plant crops after meeting the requirements of farmland soil environmental quality. In this study, the potential risk index method was selected to evaluate the ecological risk of heavy metals in soil. The emphasis of the potential risk index method was different from that of the Nemero comprehensive pollution index method, and the results were also different. The potential risk index method comprehensively considered the toxic response of heavy metals, introduced toxicity weights, and focused more on toxicology[34], the potential damage of heavy metals in soil can be easily and efficiently evaluated by comprehensive evaluation of soil ecological risk.

5. CONCLUSION

Through the investigation and sampling of the farmland soil along the Guangliji River and Jianggou River in Jiaozuo area, the content of 7 heavy metals in the soil was determined, the heavy metal pollution analysis, Nemero comprehensive pollution index method and potential ecological risk assessment were carried out, and the following conclusions were drawn:

(1) The average contents of Pb, Zn, Cd, Cr, Cu, As and Ni in the study area were all higher than the soil background values in Henan Province, and the excess rate of cadmium was 100%. The

accumulation degree of farmland along Guangliji River was slightly higher than that along Jianggou River. Compared with the screening value, Pb, Zn, Cr and Ni did not exceed the standard. The excess rate of Cd in the soil around Guangliji River was 65.2%, the excess rate of Cu was 52.2%, the excess rate of Cd in the soil around Jianggou River was 55.6%, and the excess rate of As was 5.6%.Cd in farmland soil along the two rivers exceeded the screening value by 5.7 times and 1.5 times, respectively, and was the main local pollutant.

(2) The results of single factor evaluation and comprehensive pollution index evaluation showed that Pb, Zn, Cr, Ni and As in soil were clean and pollution-free, and Cu was slightly polluted in farmland along Guangliji River. Cd was heavily polluted in the farmland soil along the Guangliji River and moderately polluted in the farmland soil along the Jianggou River.

(3) The results of potential ecological risk assessment showed that Pb, Zn, Cu, Cr, As and Ni in the study area were at a slight ecological risk level, and Cd was at a moderate or above ecological risk level. The average comprehensive potential ecological risk index of Guangliji River is 417.65, which belongs to the strong ecological risk level. The average value of comprehensive potential ecological risk index of Jianggou River is 85.79, which belongs to slight ecological risk level.

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