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# Preliminary pollution assessment and source analysis of heavy metals in agricultural soil from Xinjie Village, China

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**Abstract.** To explore the overall pollution level of heavy metals in agricultural soil and identify its main pollution sources, the selected eight heavy metals (As, Hg, Cr, Cu, Ni, Pb, Fe, and Cd) in 6 sampling sites of Xinjie Village from Qingjiang River Basin were detected. Nemerow index, Geo-accumulation index and Potential ecological risk index were used to evaluate the soil environmental quality. Results showed that the concentrations of Cd in all 6 sampling sites were relatively higher than the risk screening values for soil contamination of agricultural land. The overall heavy metal pollution level based on Nemerow index was slight. Specifically, the pollution level of Cd was moderate, while other metals were basically at clean level. Results of Geo-accumulation index showed Hg (moderately contaminated to heavily) and Cd (uncontaminated to moderately contaminated) were potential primary pollutants. The comprehensive potential ecological risk based on Potential ecological risk index was moderate, with the potential ecological risk of Cd (considerable) and Hg (moderate) higher than that of other metals. Therefore, the agricultural soil pollution in Xinjie Village was a combined pollution and mainly composed of Cd and Hg. Source analysis showed anthropogenic activities such as industrial and agricultural production were the main contributors to the accumulation of heavy metals in agricultural soil. Cd pollution mainly came from agricultural production (fertilization) and industrial emissions; the pollution source of Hg were mostly industrial emissions and the resulting atmospheric subsidence. Finally, the targeted countermeasures were developed for heavy metal pollution of agricultural soil based on the different pollution source characteristics.

## 1. Introduction

Agricultural soil is an important part of agro-ecological environment system. Heavy metals, as the typical pollutants in Chinese agricultural soil, can result in great harm to the ecological environment owing to their toxicity, persistence and bioaccumulation [1, 2]. Moreover, after the transfer of multi-media environment, heavy metal pollution in agricultural soil will eventually cause health risk to the



residents by direct or indirect exposure [3]. Therefore, to investigate and then identify the main pollution sources is the key to control heavy metal pollution in soils scientifically and efficiently.

Non-point source pollution refers to the water pollution caused by solubility or solid pollutants flowing into the receiving water body under the action of large precipitation and runoff scouring [4]. Compared with point source pollution, non-point source pollution is more difficult to control, with the pollution scale larger than point source pollution [5]. Therefore, non-point source pollution has become an important source of water-soil pollution [4, 6]. Xinjie Village is located in Qingjiang River Basin, where is rich in water resources. Also, due to the advantageous natural conditions and fertile agricultural soil, the economy of Qingjiang River Basin is dominated by agriculture, and the agricultural population accounts for more than 80% [7]. However, with the development of agriculture, agricultural poultry manure and the application of fertilizers and pesticides have brought the local agricultural non-point source pollution. In addition, in recent years, the rapid development of industry such as energy development, chemical industry and metallurgy in Qingjiang River basin has also aggravated the environmental pollution in Qingjiang River [8]. Therefore, it is of great importance to explore the overall pollution level of agricultural soil and identify its main pollution sources under agricultural non-point source pollution in Qingjiang River Basin.

The objectives of this work were to: (1) investigate the concentrations of heavy metals (As, Hg, Cr, Cu, Ni, Pb, Fe, Cd) in agricultural soils of Xinjie Village. (2) evaluate the soil environmental quality using three methods: Nemerow index, Geo-accumulation index and Potential ecological risk index. (3) comprehensively analyze the potential primary pollutants and identify corresponding potential pollution sources. (4) put forward pertinent management countermeasures based on the different pollution source characteristics.

## 2. Methods and materials

### 2.1. Study area

Xinjie Village (30°22'N to 30°23'N, 109°23'E to 109°25'E), located at the northeast corner of Tunbao township, Enshi city, Chinese Hubei province. The total area of the village is 7.45 km<sup>2</sup>, with an average elevation of 650 m, and a cultivated area of 1,264,000 m<sup>2</sup>. There are 7 groups of villagers in Xinjie Village, namely, the Kuashanzu, the Sanfangzu, the Luojiapo, the Paotongping, the Sanlongxi, the Wangjiazui and the Dishuiyan. Located in the upper reaches of Qingjiang River, the first-class tributary of the Yangtze River, Xinjie Village has abundant water resources, advantageous natural conditions and fertile agricultural soil.

### 2.2. Sampling and analysis

Combined with the characteristics of Qingjiang River Basin and local land use, soils in 6 sampling sites (S1: Kuashanzu, S2: Luojiapo, S3: Sanfangzu, S4: Wangjiazui, S5: Paotongping and S6: Sanlongxi) were collected from Xinjie Village referring to the NY/T1121.1-2006. The soil samples were collected in polytetrafluoroethylene (PTFE) bags and then transferred rapidly to the laboratory. In the laboratory, surface soils were put evenly on the plastic film to dry naturally in a cool ventilated place (No direct-sun exposure, prevent acid, alkali and other gases and dust pollution). Then, the soil samples were crushed into small pieces by using pestles and mortars. After that, samples were sifted in 10 mesh nylon sieves to remove stones and plant residue. Finally, all the samples were sifted in 100 mesh sieves and kept in the plastic bottles prior to analyses.

The pH of the soil sample was measured by pH Meter (Mettler Toledo FE20K FiveEasy, China). For the determination of total heavy metal content, 0.25 g treated samples were weighed by an electronic analytical balance (Mettler Toledo-EL204, China). After that, the samples were put into digestion vessels and digested with HCl, HNO<sub>3</sub>, HF, and HClO<sub>4</sub> by the graphite furnace digestion instrument. Then the solutions were diluted into a final volume of 50 ml with 2% (v/v) HNO<sub>3</sub>. The heavy metal contents of Cr, Cu, Pb, Zn and Cd were detected by Atomic Absorption Spectroscopy (AAS, ZEEnit700, Germany) under appropriate analytical conditions. For As and Hg content detection, 10 ml of a freshly

prepared mixed acid (1 ml high-concentration HNO<sub>3</sub>:1 ml high-concentration HCl) were added. After digestion in a boiling water bath for 2 h, the heavy metal content in the digestion solution was determined by atomic fluorescence spectrometry (AFS-9700, Haiguang Instruments Inc., China) under appropriate analytical conditions.

To ensure reliability and accuracy of analysis results, the quality assurance and quality control were assessed strictly by using blank samples, parallel samples and standard reference materials (GBW07423). The analysis results were reliable when repeat sample analysis error was below 5%, and the analytical precision for replicate samples was within  $\pm 10\%$ .

### 2.3. Soil environmental quality evaluation

**2.3.1. Nemerow index.** The Nemerow index is introduced as an integrated indicator based on the single factor index method for overall environmental quality, which can be calculated as follow formula:

$$P_N = \sqrt{\frac{IP_{av}^2 + I_{max}^2}{2}} \quad (1)$$

Where,  $IP_{max}$  is the maximum value of each single factor,  $IP_{av}$  is the average value of each single factor. Degrees of pollution based on Nemerow index were classified into five categories as shown in Table 1.

**Table 1.** Categories of pollutant pollution index.

Level	Single factor index	Pollution degree	Nemerow index	Pollution degree
1	$P_i < 1$	Clean	$P_N \leq 0.7$	Clean
2	$1 \leq P_i < 2$	Slight	$0.7 < P_N \leq 1$	Alert level
3	$2 \leq P_i < 3$	Moderate	$1 < P_N \leq 2$	Slight pollution
4	$P_i \geq 3$	Heavy	$2 < P_N \leq 3$	Moderate pollution
5	-	-	$P_N > 3$	Heavy pollution

**2.3.2. Geo-accumulation index.** The geo-accumulation index ( $I_{geo}$ ) was proposed by Muller (1969), which was widely used to study heavy metals enrichment in soil. It is calculated using the following formula:

$$I_{geo_i} = \log_2 [C_i / kB_i] \quad (2)$$

Where,  $C_i$  is the actually measured concentration of the heavy metal in the soil samples.  $k$  is corrected coefficient, which take account variation of background value caused by anthropogenic influences or lithologic variations in the soil (generally  $k=1.5$ ).  $B_i$  is the reference value of heavy metal concentration in soil.

The contamination degrees of heavy metals are classified into seven levels based on corresponding value of  $I_{geo}$ : (1) Level I:  $I_{geo} \leq 0$ , uncontaminated. (2) Level II:  $0 < I_{geo} \leq 1$ , uncontaminated to moderately contaminated. (3) Level III:  $1 < I_{geo} \leq 2$ , moderately contaminated. (4) Level IV:  $2 < I_{geo} \leq 3$ , moderately contaminated to heavily contaminated. (5) Level V:  $3 < I_{geo} \leq 4$ , heavily contaminated. (6) Level VI:  $4 < I_{geo} \leq 5$ , heavily to extremely contaminated. (7) Level VII:  $I_{geo} > 5$ , extremely contaminated.

**2.3.3. Potential ecological risk index.** The potential ecological risk index (PEI) method was established by Hakanson (1980), which was based on the principles of sedimentology. It is widely used by scholars to assess the pollution and ecological risk of heavy metal in soil/sediment. This method not only accounts for the content of heavy metals in soil, but also connects the ecological and environmental effects of heavy metals to environment toxicology.

$$E_r^i = T_r^i \times C_f^i = T_r^i \times C^i / C_i \quad (3)$$

Where,  $E_r^i$  is the potential risk of individual heavy metal,  $T_r^i$  is the toxic-response factor for a given heavy metal, and it reflects toxic level and environmental sensitivity of the heavy metal.  $C_f^i$  is the contamination factor,  $C^i$  is the actually measured concentration of the heavy metal in soil, and  $C_i$  is the reference value of heavy metal concentration in soil. For  $T_r^i$ , the values recommended by Hanson of As, Hg, Cr, Cu, Zn, Pb and Cd were 10, 40, 2, 5, 1, 5 and 30, respectively. Due to the absence of soil background values for the Qingjiang River, the soil background values for Hubei province were used.

$$RI = \sum_{i=1}^n E_r^i \quad (4)$$

Five levels of  $E_r^i$  is defined by Hanson as in Table 2.

**Table 2.** Ecological risk levels criterion.

Level	$E_r^i$ value	Extent of ecological risk of single metal	RI	Extent of ecological risk of all metals
I	$E_r^i < 40$	Low potential ecological risk	$RI < 150$	Low potential ecological risk
II	$40 \leq E_r^i < 80$	Moderate ecological risk	$150 \leq RI < 300$	Moderate ecological risk
III	$80 \leq E_r^i < 160$	Considerable ecological risk	$300 \leq RI < 600$	High ecological risk
IV	$160 \leq E_r^i < 320$	High ecological risk	$RI \geq 600$	Very high ecological risk
V	$E_r^i \geq 320$	Very high ecological risk	-	-

### 3. Results and discussion

#### 3.1. Preliminary analysis of soil environment investigation.

The results of the soil environment investigation from 6 sampling sites in Xinjie Village were shown in Table 3. Soil environmental quality-risk control standard for soil contamination of agricultural land (GB 15618-2018) stipulates different pollution risk screening values for soils with different pH values. The concentrations of Cd in all 6 sampling sites exceeded the risk screening values for soil contamination of agricultural land, and the pollution rank of each sampling site was in the decreasing sequence of S1>S6>S5>S2>S3>S4. But, the concentrations of Cd in the 6 sampling sites did not exceeded corresponding risk intervention values for soil contamination of agricultural land. The over-standard rates of Hg, As, Cr, Cu, Ni and Pb for related risk screening values and intervention values were all 0%.

**Table 3.** Test results of the heavy metal contents in soil.

Sampling site	pH	Concentration (mg/kg)							
		As	Hg	Cr	Cu	Ni	Pb	Fe	Cd
S1	4.64	12.20	0.072	56.7	16.5	28.0	28.6	3.00E-04	0.966
S2	4.50	5.55	0.043	45.8	11.5	21.5	23.7	2.88E-04	0.604
S3	5.26	10.80	0.080	49.9	14.1	22.5	24.2	2.96E-04	0.596
S4	6.17	6.80	0.167	43.3	12.4	18.5	24.1	2.94E-04	0.493
S5	8.31	10.90	0.156	57.4	21.5	25.9	30.5	3.12E-04	1.490
S6	5.67	9.99	0.226	50.0	21.6	18.5	22.5	2.60E-04	0.815

#### 3.2. Soil environmental quality evaluation

**3.2.1. Nemerow index.** According to the Soil environmental quality-Risk control standard for soil contamination of agricultural land (GB 15618-2018), the agricultural land soil pollution risk screening values were evaluated as the pollution evaluation standard values. As shown in Table 4, in terms of single-factor pollution index, the pollution level of Cd was moderate, while other metals were clean.

And the pollution level corresponding to Nemerow index was slight. The results indicated that the overall pollution was relatively light, and Cd may be the primary pollutant.

**Table 4.** Evaluation of soil heavy metal pollution based on Nemerow index.

Element	Limit value mg/kg			Single factor index	Pollution degree	Nemerow index	Pollution degree
	S1, S2, S3 (pH≤5.5)	S4, S6 (5.5<pH≤6.5)	S5 (pH>7.5)				
	As	40	40				
Hg	1.3	1.8	3.4	0.07	Clean		
Cr	150	150	250	0.31	Clean		
Cu	50	50	100	0.28	Clean	1.70	Slight
Ni	60	70	190	0.31	Clean		
Pb	70	90	170	0.30	Clean		
Cd	0.3	0.3	0.6	2.34	Moderate		

3.2.2. *Geo-accumulation index.* As shown in Table 5, except for Hg (moderately contaminated to heavily) and Cd (uncontaminated to moderately contaminated), all metals fell into uncontaminated level, indicating the overall soil environment was not bad. Hg (Level IV) and Cd (Level II) were potential primary pollutants.

**Table 5.** Assessment of soil heavy metal pollution based on  $I_{geo}$ .

Element	Background (China)/mg·kg <sup>-1</sup>	$I_{geo}$	Level	Degree
As	11.2	-1.19	I	Uncontaminated
Hg	0.065	2.89	IV	Moderately contaminated to heavily contaminated
Cr	61	-1.17	I	Uncontaminated
Cu	22.6	-0.98	I	Uncontaminated
Ni	26.9	-1.19	I	Uncontaminated
Pb	26.0	-1.65	I	Uncontaminated
Fe	2.94	-0.07	I	Uncontaminated
Cd	0.097	0.40	II	Uncontaminated to moderately contaminated

3.2.3. *Potential ecological risk index.* As shown in Table 6, Cd pollution fell into Level III, considerable ecological risk, and Hg pollution fell into Level II, moderate ecological risk. The others were all Level I, low potential ecological risk. Moreover, the comprehensive potential ecological risk was Level II, moderate ecological risk.

**Table 6.** Assessment of soil heavy metal pollution based on potential ecological hazard index.

Element	Toxic response coefficient /(mg/kg) <sup>-1</sup>	Background (Hubei)/ mg·kg <sup>-1</sup>	$E_r^i$ value	Extent of ecological risk of single metal	RI	Extent of ecological risk of all metals
As	10	11.2	7.62	Level I, Low potential ecological risk		
Hg	40	0.065	62.00	Level II, Moderate ecological risk		
Cr	2	61	1.17	Level I, Low potential ecological risk		
Cu	5	22.6	2.72	Level I, Low potential ecological risk	223.82	Level II, Moderate ecological risk
Ni	2	26.9	1.21	Level I, Low potential ecological risk		
Pb	5	26.0	4.79	Level I, Low potential ecological risk		
Cd	30	0.097	144.30	Level III, Considerable ecological risk		

### 3.3. Soil environmental quality evaluation

*3.3.1. Source analysis of heavy metals.* The main causes of heavy metal pollution in soil are natural factors and anthropogenic activities. The natural factors mainly come from the parent material, ore-forming factors and atmospheric subsidence etc. Anthropogenic activities mainly include industrial pollution emissions led by coal burning and cement production, agricultural production led by pesticide and fertilizer application and transportation emissions, etc. [9, 10] However, with the development of economy and society, the contribution of anthropogenic activities has exceeded that of natural resources. Jiang et al. concluded that the contribution rates of heavy metal pollution sources in agricultural soil in Hubei province were decreased in the sequence of agricultural production>natural causes>industrial emissions>traffic emissions, through sampling detection and PMF model analysis [11]. The results are consistent with the findings of literatures that anthropogenic activities such as industrial and agricultural production are the main contributors to the accumulation of heavy metals in agricultural soil [12, 13].

The analysis of soil environmental quality showed that Cd and Hg were the primary control pollutants. Cd is often treated as a marker element for agricultural production, especially for the use of fertilizers and organic fertilizers [14, 15, 16]. Chen et al. summarized and analyzed the related literatures of source analysis of soil heavy metal pollution in China from 2008 to 2018, and concluded that the pollution source of Cd in Hubei province mainly came from anthropogenic activities such as agricultural production (fertilization) and industrial emissions, and Hg pollution derived mainly from industrial emissions and the resulting atmospheric subsidence [10]. Hubei Province, as an important grain producing area, is a province with a large amount of chemical fertilizer applied high-ranking in China [11]. The large sown area and planting area of cash crops have led to the high amount of fertilizer input [17], which is accompanied by serious agricultural non-point source pollution. Xinjie Village is located in Hubei Province. According to the survey results, the existing cultivated land area is 1,264,000 m<sup>2</sup>, and the cash crops planting area is 2,900,000 m<sup>2</sup> (tea, oil tea, fruit, and vegetables). Therefore, the relatively high content of Cd in the heavily applied chemical fertilizer is the main source.

*3.3.2. Countermeasures.* Based on the source analysis results of heavy metal pollution in Xinjie Village, four corresponding targeted countermeasures were put forward in this study:

(1) To treat heavy metal pollution in agricultural soils by classification. Soil remediation is complex, long-term, and systematic. Soil heavy metal pollution in China has typical regional characteristics [18]. So, pollution control techniques have different effects on different regions, different types of pollutants and different land use methods. Therefore, considering the regional characteristics, it is very meaningful to treat soil heavy metal pollution by classification. For agricultural soil heavy metal pollution, such as soil pollution in Xinjie Village, the relevant government is encouraged to hire a professional scientific team to conduct a comprehensive scientific sampling and testing of the soil in the village, in order to fully grasp the pollution status of soil pollution. Then plans of soil remediation can be formulated based on the test results to identify priority control areas and pollutants and perform soil remediation efficiently.

(2) To strengthen the management of fertilizer and guide scientific fertilization. In the agricultural production, in order to improve the productivity of agricultural soils, farmers often use chemical fertilizers and pesticides blindly [19], which not only affects the quality of crops and human health, but also causes severe soil pollution. There are two main reasons for fertilizer pollution in farmland soils. On the one hand, it is because the local government lacks the corresponding management system or insufficient control. On the other hand, it is due to insufficient technical guidance for farmers. Therefore, relevant government departments should improve the management system of chemical fertilizer application according to the actual situation of agricultural production in their own regions, and enhance preventing agricultural non-point source pollution caused by chemical fertilizer abuse. In addition, the government should strengthen the guidance of farmers' scientific fertilization. It is recommended to organize experts and related staff to train farmers for scientific fertilization. For Xinjie Village, the local government should specifically manage the application of fertilizers containing Cd and Hg.

(3) To strengthen the prevention and control of industrial pollution. Pollutants in the industrial wastes can seriously affect the agricultural water resource, farmland soil and air, and directly cause heavy metal pollution. In recent years, due to the government vigorous encourage of characteristic industries, the industrial structure has been continuously optimized, and the industrial development has made great progress, including energy development, chemical industry, metallurgy and so on. Industrial development comes with the environmental pollution. Profile monitoring data have shown that the water quality of Qingjiang is decreasing year by year, and the pollution is becoming more and more serious [20]. Therefore, the relevant government departments should strengthen the whole process supervision of the industrial pollution sources in the Qingjiang River Basin, including the selection of production materials, the improvement of production technology and the limitation of pollutant discharge. The industrial emissions and pollutants should be strictly controlled to meet the emission standards

(4) To raise the awareness of soil protection and improve the public supervision mechanism. Currently in China, the public lacks a rational understanding of soil pollution. To manage and control the soil pollution better cannot rely solely on the power of the government and enterprises, and the power of the public also plays a key role. Therefore, relevant departments should raise public awareness of soil protection through public service advertisements and warning signs. It is also recommended to share information such as monitoring information, pollution source information, agricultural pollution control and remediation technologies, and the hazards and risks of soil pollution by establishing a soil pollution information platform in agricultural production areas. Let the farmers know the seriousness of soil pollution and the importance of prevention and control.

#### 4. Conclusion

The concentrations of Cd in 6 sampling sites were all higher than the risk screening values for soil contamination of agricultural land, indicating there was potential ecological risk. The evaluation results of the soil environmental quality using three methods (Nemerow index, Geo-accumulation index and Potential ecological risk index) were similar to a certain extent, which showed that the agricultural soil pollution in Xinjie village was a combined pollution mainly posed by Cd and Hg. The overall heavy metal pollution was relatively light, while Cd and Hg were potential primary pollutants. Source analysis results showed Cd pollution mainly came from agricultural production (fertilization) and industrial emissions; the pollution source of Hg were mostly industrial emissions and the resulting atmospheric subsidence. Finally, four targeted countermeasures were developed for heavy metal pollution of agricultural soil based on the different pollution source characteristics: (i) to treat heavy metal pollution in agricultural soils by classification, (ii) to strengthen the management of fertilizer and guide scientific fertilization, (iii) to enhance the prevention and control of industrial pollution in Qingjiang River Basin, (iv) to raise the awareness of soil protection and improve the mass supervision mechanism.

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