Study on Pollution Status of Cd, As, Hg and Pb in Rural Soils

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Abstract: The contents of heavy metals Cd, As, Hg and Pb in rural soils of Zhashui County (Zhujiawan Village, Xingping Village and Zhongping Village) were determined. The results showed that the contents of Cd, As and Pb in some sampling points were Slightly higher than the background value of soil elements in Shaanxi. The single factor pollution index evaluation , the ground cumulative pollution index evaluation and the potential ecological risk assessment indicated that the heavy metals in the soil showed mild pollution at some sampling points.

Soil is the basic information of agricultural production, and it is the basic environmental factor for human survival. With the rapid development of industrialization in recent years, human activities such as sewage irrigation, large-scale use of chemical fertilizers and organic fertilizers, and mining have made heavy metal pollutants enter the farmland soil environment through various channels. According to statistics, the area of heavy metal contaminated soil in China is as high as 20 million hm², accounting for 20% of the total area of cultivated land. The annual grain yield reduction due to heavy metal pollution in the soil is more than 10 million tons, resulting in economic losses of up to 20 billion^[1]. The soil pollution survey shows that the soil pollution in typical areas of Guangdong Province is mainly polluted by heavy metals such as Cd, Cu, Hg and Pb, and the over-standard rate is close to 39.8%^[2]. After more than 20 years of irrigation with cadmium-containing sewage in a farmland in Shenyang, the contaminated cultivated land reached 2,500 hm², and the cadmium content in the paddy field was 5-7 mg/kg [3]. Studies have shown that soil heavy metals such as Cu, Zn, Cd, Pb, Hg, and As will increase in different degrees after application of organic fertilizers from different sources in farmland soils. [4] The application of organic fertilizer in farmland soil can not only change the presence of heavy metals in the soil, but also affect the absorption and accumulation of heavy metals by plants [5]. Because heavy metals are not easily decomposed by microorganisms in the soil environment, and are easy to accumulate and remain in crops [6], this not only causes soil degradation, serious ecological damage, but even human health and life safety through the food chain [7]. For example, the "bone pain" that occurred in Japan from 1955 to 1972 was caused by residents eating rice with high levels of cadmium and drinking water with excessive cadmium content [8]; Similarly, residents of Minamata Bay, Kumamoto Prefecture, Japan, consume fish and

contaminated with mercury wastewater, causing nearly 10,000 people suffering from central nervous system diseases - leeches ^[9]. It can be seen that the pollution of heavy metal in soil is very serious, and the area polluted in recent years has increased year by year. Therefore, it is very necessary to evaluate the heavy metal pollution of soil. At present, most of the researches focus on heavy metal pollution in sensitive areas such as mining areas, sewage irrigation areas and power plants. There are few studies on the evaluation of heavy metals in rural soils. This paper selects Zhujiawan Village, Xingping Village, Zhongping Village as the research object, which was in order to provide a reliable theoretical basis for the sustainable development of rural farmland soil.

1 Materials and methods

1.1 Sample Collection

Soil sample were obtained from Zhujiawan Village, Xingping Village, and Zhongping Village of Zha shui in March 2017. According to the requirements of the Technical Specifications for Soil Environmental Monitoring, combined with the shape of the study area within 50m around each sampling point, Surface soil samples (0 - 20 cm) were collected for a total of 17, all the samples were obtained from five subsamples with an "S" sampling procedure. Use the quartering method to keep about 1kg, seal it in the ziplock bag and bring it back to the laboratory to avoid sample contamination. The sample was naturally air-dried to remove foreign matter such as gravel, and through a 0.149 mm nylon sieve for storage. The location of the study area is shown in Figure 1.



Fig 1 Location of the study area

1.2 Sample analysis

Cd determination of soil samples: 0.2000 g of soil samples were accurately weighed in polytetrafluoroethylene, digested with HCl $_{\circ}$ HNO $_{3}$ and H $_{2}$ SO $_{4}$, and the organic phase was determined by flame atomic absorption spectrophotometer after KI-MIBK extraction.

Cr determination of soil samples: accurately weigh 0.2000 g of the sample in 50 mL of polytetrafluoroethylene hydrazine, add HCl to the initial decomposition, digest with HNO₃, HF and HClO₄, and then measure with a flame atomic absorption spectrophotometer.

As and Hg determination of soil samples: 0.5000 g of soil samples were accurately weighed in a 50 mL stoppered colorimetric tube, and aqua regia was added to the water bath for 2 hours, and the supernatant was taken and measured with an AFS-2202E atomic fluorescence spectrometer.

The acid purity used in the experiment was excellent and pure. The experimental method was analyzed by the National Soil Composition Analysis Standard (GSS-8) for quality control. The standard samples used in the test were prepared using national standard materials.

Table 1 Description of sampling point

	Location	Depth	Soil color
Zhujiawan Village	E109°01′21″ N33°48′29″	0—20cm	Yellow
Xingping Village	E109°26′10.43″ N33°30′09.49″	0—20cm	and brown sand
Caopingzhen Village	E109°24′15″ N33°44′01″	0—20cm	

1.3 Data analysis methods

(1) Single factor pollution index and classification standard

The expression of the cumulative index is shown in equation (1)

$$I_{Geo} = Log_2(\frac{c_1}{kB_1})$$
(1)

where I_{Geo} is the Ground accumulation index; c_i is the measured concentration of the heavy metal i in soils, mg/kg; B_i is the geochemical background of the heavy metal i; k is a constant, generally k=1.5, according to the magnitude of the value, the degree of heavy metal pollution divided into 7 levels, as given in Table 2.

Table 2 Accumulated index classification of heavy metals

Ground accumulation index	Level	Degree of pollution
I _{Geo} ≥5	6	Extremely contaminated
$4 \le I_{Geo} < 5$	5	Severe pollution
$3 \leq I_{Geo} < 4$	4	Strongly contaminated
2≤ <i>I_{Geo}</i> <3	3	Moderately to strongly contaminated
1≤ <i>I</i> _{Geo} <2	2	Moderately contaminated
0≤ <i>I_{Geo}</i> <1	1	Uncontaminated to moderately contaminated
$I_{Geo} < 0$	0	Uncontaminated

(2) Potential ecological risk index

Potential ecological risk index can be used to determine the potential risk due to exposure to ecological sensitivity, concentration and toxicity of heavy metals (Nabholz, 1991; Douay et al., 2013). It is also regarded as a comprehensive potential ecological risk assessment, Eir, which is the sum of the potential risk of individual metal element. It represents the sensitivity of the biological community to the toxic substance and illustrates the potential ecological risk caused by the overall contamination. The estimation of total risk index (RI) of PERI was calculated using Eq. (1) as proposed by Guo et al. (2010) and was first introduced by Hakanson (1980):

$$C_{f}^{i} = \frac{c_{s}^{i}}{c_{n}^{i}}$$
 (1); $E_{r}^{i} = T_{r}^{i} \times C_{f}^{i}$ (2);

$$RI = \sum_{i=1}^{n} E_r^i$$
 (3)

Among them, RI is the potential ecological risk index of various heavy metals; E_r^i is the potential ecological

risk index of heavy metals i; C_f^i is the heavy metal coefficient in soil, the background value of soil heavy metals in Shaanxi Province is used in the research; C_s^i is the measured value of soil heavy metal i, mg/kg; is the toxicity response parameters of heavy metals i, according to the standards established by Hakanson, the toxicity response coefficients of heavy metals involved in this study are: Hg = 40, Cr = 2, Cd = 30, As = 10, Pb = 5, Cu = 5, Zn = 1, Ni = 5. The classification results of the potential ecological risk index method are shown in Table 4.

 Table 4
 Classification criteria of potential ecological risk index

Ecological risk	Low risk	Mode rate risk	Consider able risk	High risk	Significantly high risk
E^{i}_{r}	<40	40-80	80-160	160- 320	>320
RI	< 150	150-3 00	300-600	≥60 0	

2 Results

2.1 Descriptive statistics of soil heavy metal content

The descriptive statistics of soil heavy metal content in the study area are shown in Table 5. It can be seen from Table 5 that the Cd content in the sampling area of Zhujiawan Village is slightly higher than the background value of soil elements in Shaanxi, and the average value is 0.13mg/kg. The variation range of Cd, Cr, Hg and As in the region is relatively large, and the coefficient of variation of Cd is 66.67%, indicates that there is a high Cd content in individual areas, and the over-standard ratio of sampling points is analyzed. The over-standard rate of Cd sampling points is 50%; the corresponding elements of Cr, Hg and As are lower than those of Shaanxi soil elements. The background values have coefficients of variation of 22.25%, 20.00%, and 24.05%, respectively.

The contents of Cd and As in the sampling area of Xingping Community were higher than those in Shaanxi, and the mean values were 0.12mg/kg and 20.0mg/kg, respectively. The variation range of Cd was larger, and the coefficient of variation was 54.55%. The Cd content of individual points in this area also has a high phenomenon; the variation coefficients of Hg and Cr contents of other elements are small, and the coefficient of variation is 33.33% and 24.12%, respectively.

The Hg content of each sampling point in the sampling area of Zhongping Community was slightly higher than that of Shaanxi soil element. The average content of the Hg was 0.17mg/kg, and the average contents of other elements Cd, Cr and As were 0.10mg/kg and 58mg /kg, 12.6mg/kg respectively., where As has a large change range, and the coefficient of

variation is 40.32%.

2.2 Soil single factor pollution index method evaluation

It can be seen from Table 6 that the average single-factor pollution index of heavy metals Cd, Cr, Hg and As in the surface soil of the study area is less than 1, and the corresponding pollution level is clean, indicating that the heavy metal content above the research area is low, and the pollution level is judged as Safety, indicating that the area Cd, Cr, Hg, As pollution is light, not reaching the warning level.

2.3 Evaluation of the cumulative pollution index

Figure 2 shows the cumulative pollution index analysis of the study area. It can be seen from the figure that only the heavy metal As of Xingping Community and the Hg of Zhongping Community have a cumulative pollution index greater than 1, which is mildly polluted. The cumulative pollution index of the remaining elements is less than 1, which indicates that the soil environment quality of the study area is good and it is not seriously polluted by heavy metals Cd, Cr, Hg and As.

2.4 Potential ecological risk assessment of heavy metals

It can be seen from Fig. 3 that from the analysis of single heavy metal elements, the potential ecological risk grades of heavy metals Cd, Cr, Hg and As in the surface soil of Zhujiawan Village and Xingping Town of Yingpan Town are Grade A (slightly harmful). The potential ecological risk level of surface soil Hg in Zhongping Community is Grade B (medium hazard), and the potential ecological risk level of Cd, Cr and As is Grade A (minor degree of hazard).

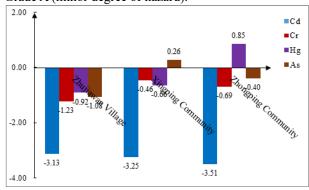


Figure 2 Cumulative pollution index at each sampling point

Standard Background Standard Variation Sampling site Element Range Mean deviation coefficient % Value Value 0.03~0.28 0.13 0.122 0.3 Cd 0.08 66.67 28~53 40 8.9 22.25 69.3 200 Zhujiawan Cr Hg Village $0.03 \sim 0.06$ 0.05 0..01 20.00 0.085 0.5 4.6~10.3 7.9 1.9 24.05 30 As 16.0 $0.04 \sim 0.20$ 0.12 0.0654.55 0.1220.3 Cd 46~95 68.0 16.4 24.12 69.3 200 Cr Xingping Community $0.04 \sim 0.10$ Hg 0.06 0.02 33.33 0.085 0.5 16~24 20.0 3.2 30 As 16.00 16.0 Cd $0.08 \sim 0.14$ 0.10 0.02 20.00 0.122 0.3 Zhongping Cr 46~71 58 9.23 15.91 69.3 200 Community Hg $0.12 \sim 0.23$ 0.17 0.04 23.53 0.0850.5 As 6~21 12.6 5.08 40.32 16.0 30

Table 5 Descriptive statistics of soil heavy metal elements in the study area

Table 6 pollution index of soil heavy metals in study area

Sampling site	Single factor index	Elements	Cd	Cr	Hg	As
Zhujiawan Village P _i		Minimum	0.03	0.15	0.02	0.23
	\mathbf{P}_{i}	Maximum	0.28	0.28	0.04	0.52
		Mean	0.12	0.21	0.03	0.39
Xingping Community P _i		Minimum	0.04	0.24	0.03	0.80
	P_{i}	Maximum	0.20	0.50	0.07	1.20
	•	Mean	0.11	0.36	0.04	1.00
Zhongping Community	P_{i}	Minimum	0.08	0.26	0.08	0.30
		Maximum	0.14	0.37	0.15	1.05
		Mean	0.10	0.31	0.11	0.63

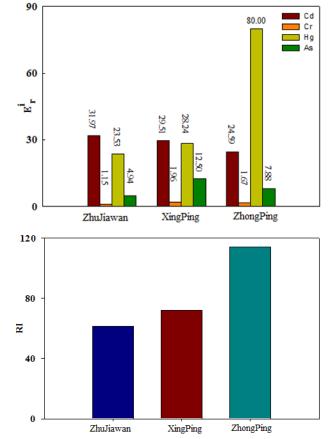


Figure 3 Potential risk factors for heavy metals at each point

3 Discussion

Soil heavy metal content is closely related to soil parent soil texture, organic matter industrialization, urbanization and rural intensification [10]. Fan Wei et al. conducted a statistical analysis of the concentrations of Cr, Cu, Pb, Zn, Ni, Cd, Hg and As in the farmland soils of 8 cities in China. The heavy metal content of farmland soils in most cities was higher than the soil background value [11]. With the improvement of living standards in China, the output of rural garbage has increased year by year. According to statistics, the annual amount of domestic garbage produced in rural areas in China has reached 300 million tons [12]. However, these wastes have not been properly managed, and a large amount of heavy metals in the leachate are likely to cause soil and groundwater contamination [13].The research WangZhenzhong et al shows that heavy metals in waste are easily enriched in the soil and cause serious pollution of heavy metals in the soil around the dumping area[14].In addition, sewage irrigation, long-term application of chemical fertilizers and organic fertilizers can cause serious pollution of heavy metals in farmland soils. For example, Chen Fang et al [15] pointed out the application of chemical fertilizers, especially phosphate fertilizer, as the application period increases, the heavy metals As, Hg, Cd and Pb all show an upward trend in "Variation of Soil heavy metal Contents in a Long-term Fertilization Experiment". Goss et al [16] have shown that organic fertilizers also contain different levels of heavy metals in addition to the nutrients necessary for soil, especially organic fertilizers used as raw

materials for livestock and poultry. When applied, soil heavy metal content is inevitably increased. Zhou Zhenmin and other studies have shown that [17] farmland sewage irrigation will carry a certain amount of heavy metals, and near the irrigation water source, heavy metal pollution is more serious.

The single factor pollution index evaluation in this study area shows that heavy metals Cd, Cr, Hg and As are safety. The cumulative pollution assessment index method indicates the heavy metal As in Xingping Community and the Hg in Zhongping Community are greater than 1, both are mildly polluted. the potential ecological risk study of heavy metals indicates that Cd, Cr, Hg, and As are mildly polluted in Zhujiawan Village and Xingping Community, and Hg in Caoping Community is moderately polluted. The remaining heavy metals are all slightly polluted. After surveys of farmers in Zhashui, nearly 90% of farmland applied agricultural fertilizers, and 95% of farmers did not involve sewage irrigation. Since the reform and opening up, the application of chemical fertilizers to increase crop yield has become an indispensable means. Thus, it can be seen that the slight pollution of heavy metals of Cd, Cr, Hg and As in the study area may be caused by the long-term migration of heavy metals in the domestic landfill leachate with rain.

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