The influence of migration on the reconstruction area of soil contaminated by complex heavy metals

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Abstract. In the heavy metal compound pollution area, the isolation and repair technology was used to seal the fixed contaminants. And then, the land organic reconstruction carried out. In order to test the isolation effectiveness of reconstructed land, two experiments have been carried out. There were the migration status of heavy metals in reconstruction soil profile and its effects on crops, respectively. The contents of the heavy metal pollutants such as Hg, Cu, Cd, Zn, Pb, As, Cr and Ni were studied. The results showed that Hg, Cu, Cd, Zn and Pb were the main heavy metals that caused pollution in the study area. Besides, the concentration of Pb was very serious. After two years of planting, the content of heavy metals in each layer of the reconstructed and profile were lower than that of the soil environmental quality standard (GB 15618-1995). The migration and accumulation of heavy metals on the various soil profiles were not found. And the edible part of corn and peanuts planted which were planted in the reconfiguration soil profile could conform the food safety requirements.

1. Introduction

China was rich in mineral resources, and the heavy metal pollution caused by the exploitation of mineral resources was very common in the mining process [1]. Heavy metal polluted soil and high risk area had emerged in the mining area and the surrounding area. Jiao. et al. investigated the pollution of farmland soil in the northern Guangdong mining area, indicated that the Cd pollution was serious and the Ni contamination existed to varying degrees. In addition to Cu and Zn in the brown rice, other heavy metals with different concentrations were also detected [2]. On the basis of investigating heavy metal pollution and plant accumulation in farmland soil in great Baoshan mining area, Zhang. et al. found that the contents of Cu, Pb and Cd in soil samples were much more than the grade II standard of soil environmental quality [3].

Tongguan, located at the E110°09′32″~110°25′27″ and the N34°23′33″~34°39′01″. The north of Tongguan was near the Yellow River, and its south near Qinling Mountains, containing Au, Ag, Pb and so on. It was famous for rich reserves of gold and long history of mining. As the pillar industry of Tongguan, the gold industry contributed more than 70% of the county's financial revenue. While the
frequent mining activities were bringing huge economic benefits, and at the same time, left many problems such as heavy metal pollution and so on.

In the heavy metals compound polluted area, the pollutants were buried and fixed by isolation and repair technology. The structure of land profile was reconstructed on the isolation layer to achieve the purpose and requirements of isolating pollutants, protecting the structure and function of the isolation layer, and meeting the cultivation of the reconstructed profile. Under the conditions of isolation, the release and migration of heavy metals was more complex than in natural conditions. The types of material, heavy metal content, physical and chemical properties, and the thickness of section layer were related to the reconstruction of soil profile, and it was also closely related to the properties of the isolation layer. On the one hand, the profile reconfiguration leaded to the change of temperature, humidity, pH and other environmental conditions. On the other hand, the composition of the isolation layer and the tailings containing heavy metals might be neutralized, adsorbed, and ion exchange, and so on. These chemical reactions have an impact on the original mineral components and their occurrence state in pollutants, and inhibited the diffusion and migration of heavy metals. It was great significance to study the effect of isolation and repair technology by means of monitoring and evaluating the heavy metals contents of each layer in the reconstructed soil profile regularly.

2. Materials and Methods

2.1. Experimental method

In order to fully simulate the migration of heavy metals in the reconstructed profile of composite contaminated soil, the in situ field experiment was carried out. Firstly, the compound heavy metals pollutants was compacted, and then covered the isolation layer. Specifically, the pure soil layer and the farming soil layer were spread out respectively. The pure soil layer thickness was 40 cm, and its compaction coefficient should not be less than 0.83. The thickness of the farming soil layer should be 30 cm with packing naturally. The reconstituted soil profile configuration as shown in Figure 1. In order to compare the difference of land quality between the application of isolation technology and the uncontaminated. Set the reconstituted soil profile as the experimental group, and the contrast was treated as an unpolluted ordinary farmland, which was recorded as CK. The plane size of each cell was 3 m×3 m. According to the site conditions of the community, the uniformity of light, micro terrain and other factors were considered.

The crops were planted for two years in the natural rainfall situation. During this period, soil samples were collected regularly to determine the content of heavy metals in the farming and pure soil layers of the reconstructed soil. The migration of the heavy metals in the soil profile and the accumulation in the plant samples were investigated and evaluated.

2.2. Sample collection

The peanuts were planted in the first year, with planted the corn in the next year. After the crop harvest, the soil and plant samples were collected. According to the requirements of the technical specification for soil environmental monitoring, the sampling points of surface soil samples or heavy metal pollutants were mainly in one place. As a fixed-point sampling location, the "plum blossom sampling" was used within the range of 5 m, and the 2–3 subsample combined into a mixed sample, retained the sample weight of 1 kg. The sampling depth was 0 cm~30 cm, 30 cm~50 cm, 50 cm~70 cm from top to bottom successively. The location of the sampling point should be recorded accurately.

2.3. Sample processing and determination

2.3.1 Treatment and determination of soil samples. The soil and heavy metal pollutants samples were dried by natural wind, removed sundries and grind, sieved the 0.149 mm nylon mesh, determined the following indicators: pH and Hg, Pb, Cd, As, Cr, Zn, Cu, Ni. And the samples were determed in accordance with the relevant standards, such as GB/T 17141-1997, HJ 491-2009, GB/T 17139-1997,
GB/T 17138-1997, GB/T 22105.1-2008, GB/T 22105.2-2008 and so on.

2.3.2 Treatment and determination of plant samples. Washed the crop seeds with tap water, and rinsed and dried with deionized water. Seeds were placed at 105 °C to kill for 30 min, and then adjusted the temperature to 75 °C to dry to the constant weight, which was recorded dry weight (g). Samples were pulverized with the agate mortar, sieved the 0.25 mm nylon mesh. Determined the following indicators: Hg, Ni, Cd, As, Pb. The samples were determined in accordance with the relevant standards, such as GB 5009.17-2017, GB 5009.123-2014, GB 5009.138-2017, GB 5009.11-2014, GB 5009.15-2014, GB 5009.12-2017.

2.4. Evaluation method of heavy metal pollution
The soil environmental quality standard included three grades, of which the grade II was the soil limited value for the protection of agricultural production and the maintenance of human health [4]. GB15618-1995 was used as a basis for evaluation of heavy metal pollutants and the accumulation of heavy metals in the reconstructed profile. The soil samples of heavy metal pollutants and regular monitoring were evaluated using the method of "accumulative pollution index".

The contents of heavy metals in the seeds of the harvested crops were compared with those in the normal cropland, and the effectiveness of the isolation treatment technology was evaluated. The safety of edible parts were evaluated by comparing the limit of heavy metals contents in GB 2715-2016 and GB 2762-2017.

3. Discussion

3.1. Type and content of heavy metals in the samples
According to the standard method, 30 samples of heavy metal pollutants were collected. And the content of 8 common heavy metals were measured, such as Hg, Cr, Ni, Cu, Cd, Zn, As and Pb. Evaluation of the results of heavy metals in samples by using the "accumulative pollution index". Descriptive statistics of heavy metal pollutants were shown in Table 1. Table 1 showed that in the construction area, the content of As in heavy metal pollutants was lower than the background value of soil elements in Shaanxi. The contents of Cr, Ni, Cu, Zn, Cd and Pb changed limitedly, and the coefficient of variation were less than 10%. The change of Hg content was more than 50%, with most of the high content of points. It showed that the Hg was greatly influenced by human activity. The average contents of Hg, Cu, Zn, Cd and Pb were all higher than the background values of soil elements in Shaanxi. The average contents of Hg, Cu, Cd and Pb were higher than the grade II of GB15618-1995(pH>7.5), with 1.29~8.6 times more than the standard limit, respectively. The contents of Cd and Pb exceeded the standard significantly. Analysis of the excess scale from the sampling point, Hg, Cd and Pb had the higher standard exceeding ratios of 68.3%, 46.1% and 16.9%, respectively.

Table 1. Descriptive statistics of heavy metal pollutants.

| Element | Range   | Mean  | Standard deviation | Variation Coefficient (%) | Shaanxi soil element background value | Soil environmental quality standard grade II (pH>7.5) |
|---------|---------|-------|--------------------|----------------------------|--------------------------------------|-----------------------------------------------|
| Hg      | 0.69~7.82 | 4.65  | 2.96               | 63.66                      | 0.06                                 | 1.0                                           |
| Cr      | 51.01~58.68 | 53.46 | 3.70               | 0.07                       | 55.00                                | 250                                           |
| Ni      | 7.06~10.77  | 8.60  | 19.40              | 2.26                       | 24.00                                | 60                                            |
| Cu      | 110.56~145.63 | 129.01 | 14.40             | 0.116                      | 17.90                                | 100                                           |
| Zn      | 47.13~492.08 | 197.74 | 208.15            | 1.06                       | 45.30                                | 300                                           |
The contents of heavy metal elements in the soil of Guanzhong area of Shaanxi Province were used as the background value [5]. The application of the "ground cumulative pollution index method" to the heavy metal content of pollutants, the results of the evaluation were shown in Figure 2. According to the figure 2, it was known that the cumulative index of the 8 kinds of heavy metals from large to small was Pb(7.52)>Cu(2.35)>Zn(2.20)>Hg(2.01)>Cd(1.49)>Cr(-0.56)>Ni(-1.90)>As(-2.76) in turn. Inside, Cd was enriched with partial moderate pollution. The concentration of Hg, Cu and Zn were all moderate pollution, and the concentration of Pb in this area was extremely serious. There were no enrichment of Cr, Ni and As at 100% sampling points. The ratio of Hg, Cd, Cu, Zn and Pb to moderate concentration were 32.4%, 23.1%, 30.8%, 30.8% and 23.1%, respectively. The Cd of the 15.3% sampling points were partial to moderate enrichment. For Cu, 23.1% of the sampling points were heavily enriched. And for Pb, 53.8% sampling points were seriously enriched. According to data analysis, the cumulative effect of Hg, Pb, Cu, Zn and Cd in heavy metal pollutants were obvious. Many reasons accounting for this were as follows: first, the Gold deposits belong to rock gold deposits. The main associated elements were Pb, Cu, Pb and Zn, due to their metallogenic characteristics and associated metal mineral contents. Second, a variety of flotation agents were added to, which resulted in the high content of heavy metal pollutants in the mineral processing. Lastly, in Tongguan area, amalgamation, cyanidation and other mineral processing technology and gold extraction process were applied.

![Figure 1. The reconstituted soil profile configuration diagram](image1)

![Figure 2. The average $I_{Geo}$ of heavy metals](image2)

### 3.2. The change of heavy metal content in the reconstructed soil profile

Soil was complex and spatiotemporal variability due to the influence of soil matrix, climate, and biological factors [6]. Two aspects of variation in the plane distribution and variation in the vertical profile of the soil. The distance between the land and pollution sources, the way of using land and the utilization time determined the distribution and pollution degree of the heavy metal elements in the soil [7]. Under the influence of point source pollution, the impact of solid pollution sources was the highest, followed by liquid, and the smallest gas. The concentration of heavy metals in soils was high, with the influence of pollution decreasing gradually with increasing distance. Linear pollution sources
such as rivers and irrigation channels, soil pollution levels of heavy metals were generally decreasing from center to both sides. Non-point source pollution was mainly influenced by wind direction, industrial layout and other factors. Heavy metals in agricultural land were often affected by the combined effects of single or multiple sources of pollution, such as industry, transportation and irrigation. It was beneficial to control the pollution of heavy metal pollutants and restore the land ecology by using the method of reconstruction for the composite contaminated soil. While eliminating point source pollution, pollution caused by traffic or irrigation should be prevented. Taking the planting mode, planting time and the distance between the section and the heavy metal contaminants into consideration, if the heavy metal contaminants could be strictly isolated, there were no adverse effects on the reconstructed soil profile. However, regular monitoring and testing were still needed.

Different land use patterns led to different contents of heavy metal elements in soils. Heavy metals in soil were mainly concentrated in the 20–60 cm soil layer, and there were some differences in the vertical distribution of heavy metals content. Therefore, it was very important to sample and monitor the depth of the soil layer of the reconstructed profile. According to the experimental design, 30 samples of soil samples were collected to determine the content of 8 heavy metal elements in soil samples. The median value of heavy metal content were shown in Table 2.

Table 2. Heavy metal content in reconstructed profile of compound polluted soil.

| Treatment                 | Profile depth (cm) | The median heavy metal content (mg kg⁻¹) |
|---------------------------|-------------------|-----------------------------------------|
|                           |                   | Hg  | Cr  | Ni  | Cu  | Zn  | As  | Cd  | Pb  |
| CK                        | 0–30              | 0.22 | 51.4 | 29.0 | 31.8 | 53.7 | 3.3  | 0.19 | 31.6 |
|                           | 30–50             | 0.38 | 46.2 | 30.4 | 54.3 | 43.2 | 2.7  | 0.16 | 51.1 |
|                           | 50–70             | 0.32 | 55.7 | 31.3 | 45.2 | 49.1 | 4.9  | 0.19 | 49.0 |
|                           | Mean              | 0.29 | 51.1 | 30.1 | 42.1 | 49.4 | 3.6  | 0.18 | 42.1 |
| Isolation treatment       | 0–30              | 0.29 | 38.1 | 32.8 | 36.5 | 31.9 | 2.8  | 0.12 | 41.3 |
|                           | 30–50             | 0.29 | 43.6 | 27.8 | 41.0 | 37.4 | 3.3  | 0.15 | 42.6 |
|                           | 50–70             | 0.32 | 50.6 | 33.6 | 44.6 | 34.5 | 3.3  | 0.17 | 46.4 |
|                           | Mean              | 0.30 | 43.2 | 31.6 | 40.1 | 34.2 | 3.1  | 0.14 | 43.1 |
| Soil environmental quality grade II | 1.0 | 350 | 60  | 100 | 300 | 20  | 0.6  | 350 |

After two years of cultivation, the contents of heavy metals in reconstructed soil profiles were compared with those of soil environmental quality standard grade II and the contents of heavy metals in corresponding soil profiles in CK. The results showed that the contents of heavy metals in the layers of reconstructed soil profile were all lower than GB 15618-1995, and accumulation of heavy metals on the soil profiles was not observed. The average value of heavy metal content at per unit thickness of soil were calculated, and compared the reconstructed soil profile with those of the control soil profile. The results showed that the contents of Cr, Cu, Zn, As and Cd in different profile depth were all lower than the CK. The contents of Hg, Ni and Pb were slightly higher than CK, increased by 2.5%, 5.1% and 2.3%, respectively. Combined with the results that Hg, Cd, Cu, Zn and Pb in pollutants were the main heavy metals that cause pollution, we can see that most of the heavy metal elements were effectively isolated. However, the contents of Hg and Pb were not significant compared with CK. There was no obvious change in the content of heavy metals in the sections of the reconstructed profile, which indicated that the effect of heavy metal blocking was good. However, in order to prevent the
diffusion and migration of heavy metals, the contents of heavy metals in all layers of reconstructed soil profiles should be paid close attention to.

3.3. Heavy metal content in the seeds
In order to evaluate the effectiveness of isolation and reconstruction techniques, the accumulation of heavy metals in crops grown in soil were monitored, and a total of 20 samples of peanut and maize were collected. The average content of heavy metals were shown in Table 3.

| Treatment                  | Sample  | Average value of heavy metal content (mg kg⁻¹) |
|----------------------------|---------|-----------------------------------------------|
|                            |         | Hg  | Ni  | As  | Cd  | Pb  |
| CK                        | Corn a  | ND  | 0.42 | 0.02 | 0.03 | 0.25 |
|                            | Peanut b | ND  | 0.55 | 0.14 | 0.06 | 0.32 |
| Isolation treatment        | Corn a  | ND  | 0.42 | 0.03 | 0.02 | 0.25 |
|                            | Peanut b | ND  | 0.52 | 0.14 | 0.07 | 0.24 |
| Food safety limits         |         | 0.02 | 1.0  | 0.5  | 0.1  | 0.5  |

Table 3. Content and limit of heavy metals in edible part of cropping plants.

| Treatment                  | Sample  | Average value of heavy metal content (mg kg⁻¹) |
|----------------------------|---------|-----------------------------------------------|
|                            |         | Hg  | Ni  | As  | Cd  | Pb  |

a The element content was extremely low, exceeding the detection limit of 0.003 mg kg⁻¹.
b The element content was extremely low, exceeding the detection limit of 0.003 mg kg⁻¹.

The concentration of heavy metals in plants had a certain correlation with the content of heavy metals in the soil grown by plant roots. By monitoring the content of heavy metals in plants, it could indirectly reflect the heavy metals contents of soils. Isolation treatment compared with the CK of planted crops. There were no obvious changes in the content of Hg, Ni and Pb in corn grains. While, the content of As was slightly higher than CK, Cd content slightly lower. However, the contents of Hg, As, Ni and Pb in peanut grains were at a same level or lower than CK, Cd content slightly higher. By means of comparison, it was found that there was no significant difference in the contents of heavy metals in the planted crops between the reconstructed soil profiles and the CK. The contents of heavy metals in the seeds of corn and peanut under all treatment conditions were significantly lower than the content limit of GB 2715-2016 and GB 2762-2017.

4. Conclusion
1) The following conclusions were drawn by the analysis of heavy metal pollutants in the study area by the method of "accumulation pollution index": As was not a typical polluted metal in the study area. Hg, Cu, Cd, Zn and Pb were the main heavy metals that caused pollution in the study area. Inside, the concentration of Pb was very serious, and Pb was the typical pollution element in the study area.
2) After two years of cultivation, the contents of heavy metals in the layers of reconstructed soil profiles were all lower than the grade II of the "Soil Environmental Quality Standard" (GB 15618-1995). The migration and accumulation of heavy metals on the various soil profiles were not found. There was no significant change in the content of heavy metals in different depth of soil profile.
3) The content of heavy metals in the edible parts of corn and peanut planted in the compound pollution reconstructed soil profile were lower than the food safety limits. In other words, the crops planted in the soil profile reconfiguration were in accordance with the food safety requirements.

References
[1] TIAN K, YANG J, SUN Z J, et al. 2017, Preparation of Soil Certified Reference Materials for Heavy Metals in Contaminated Sites [J]. Rock and Mineral Analysis, 36(1): 82-88.

[2] JIAO H P, ZHU H R, JIANG H Y, et al. 2017, Distribution Characteristics and Correlations of Heavy Metals in Contaminated Farmland Soils in Yuebei Mining Area [J]. Chinese Agricultural Science Bulletin, 33(19):93-100.

[3] ZHANG H, JIN Q W, HUANG R L, et al. 2017, Characteristics of Heavy Metal Pollution in Agricultural Soils and Bioaccumulation in Plants of Dabaoshan Mine [J]. Soils, 49(1):141-149.

[4] ZHANG M. 2012. Study on the changes of soil quality after reclamation of coal mining subsidence area-A case study of reclaimed area filling with fly ash in Jiawang, Xuzhou, China [D]. Chinese academy of agricultural sciences.

[5] Xue C Z, Xiao L, Wu Q F, et al. 1986. Studies of background values of ten chemical elements in major agricultural soils in Shaanxi Province [J]. Acta universities agriculturalis boreali-occidentalis (NATURAL SCIENCE EDITION), (3):30-53.

[6] DUAN H M. 2012. The study on heavy metal pollution of urban soils in YongKang [D]. Zhejiang Normal University.

[7] LIU J F, GU N, ZHANG K H. 2012. Progress and prospect of soil heavy metal spatial differentiation and migration [J]. Geography and Geo-Information Science, 28(2):99-103.