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Study on The Transport and Transformation of Heavy Metal Lead from Agricultural Land in An Abandoned Mining Area in Southwestern Yunnan

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Abstract: In this paper, the heavy metals in the agricultural land around an abandoned mine in southwest Yunnan Province were taken as the object of study, 15 samples of topsoil, middle soil and deep soil were collected, and 5 maize plants were randomly selected in the soil sampling points to study the migration and transformation of heavy metal lead in the soil-maize system in the agricultural land around the abandoned mine. The results showed that the soils in the study area were enriched with heavy metal Pb, which was generally expressed as surface soil > middle soil > deep soil; the migration capacity of heavy metal Pb in different organs of maize: roots > leaves > stems and kernels. The results of the study can be used as a basis for judging the migration and transformation of heavy metals in soil-crop systems, providing new theoretical support for the migration of heavy metals in soils around abandoned mining areas, and promoting the ecological remediation of heavy metal pollution in agricultural land.

Keywords: Abandoned mine site; Agricultural land; Heavy metals; Migration and transformation.

1. The Context of the Study

As a large agricultural country, China has a vast area of arable land, which covers 7 per cent of the world's arable land, and the output value of our arable crops is also much greater than that of other industries[1]However, according to the results of the National Soil Pollution Survey Bulletin issued by the Ministry of Environmental Protection in 2014, the quality of soil in China has declined, with serious contamination of soil on agricultural land and extremely prominent soil environmental problems on industrial and mining waste land, with an exceedance rate of 19.4 per cent, and the most important pollutants being heavy metals[2]. At present, with the continuous development of China's economy, the development of mineral resources, metal smelting, sewage irrigation and the irrational application of chemical fertilizers and pesticides have led to the continuous enrichment of heavy metals in agricultural soils[3]Heavy metal pollution is also becoming more and more obvious, and heavy metal enrichment in the soil causes soil pollution, and the problem of soil heavy metal pollution has become a topic of key concern for all mankind[4]。

In the study of heavy metal pollution in mines, the key heavy metal elements are: Cu, Pb, Zn, Co, Au, Ag, Cd, As, etc. The heavy metal elements are very different from other pollutants, and most of the heavy metal pollutants will remain in the soil for a long time[5]. On the same level as Gong Zi[6]In the study of the impact of human activities on the quality of the soil environment and countermeasures, it is pointed out that the area of basic farmland in China is about 100 million hectares, and the area of arable land is polluted by 26.67 million hectares, of which 20 million hectares are polluted by heavy metals, thus appearing a large number of crops contaminated by heavy metals. Xiang Meng[7]We investigated the distribution pattern of heavy metal pollution in soil profile and pore water in the lead and antimony smelting area of Guangxi. Heavy metal lead is mainly found in the soil in the form of specialized adsorption state, and it will be more easily absorbed by plants when the form is transformed into the organic adsorption state, and it will be more easily absorbed by plants when the form is transformed into the organic adsorption state[8]。

Human activities affect the soil in many ways, including industrial and mining activities such as mining, transportation, smelting and other processes, will produce heavy metal pollution, of course, in the process of crop cultivation pesticide unreasonable application will also produce a certain amount of heavy metal pollution. Lead and zinc ore is one of the important strategic mineral resources in China, in the lead and zinc tailings open dumps in the lead, zinc and other heavy metal content, heavy metal-containing pollutants through the mine washing wastewater runoff, dust, rainfall and other ways to enter the infiltration of the nearby agricultural land soil, a serious impact on the structure and function of the agricultural soil, so that the mining area around the agricultural land by the pollution of heavy metals, the heavy metal pollution[9]. Feng Qianwei[10]When analyzing the source of heavy metals in the soil near a lead-zinc mine in western Guizhou, etc., it was found that the source of Pb, Zn, As and Cd in the soil would be affected by the mining process of the surrounding mining industry. According to Yang Weiwei[11]et al. showed that the Pb content in various organs of maize was maize root system > maize leaf > maize stem > maize grain, and the distribution pattern of Pb content in various soil layers was surface soil > middle soil > deep soil.

Mingshan Zhang[12]et al. showed that the content of lead in plants is related to different organs of the plant, and that, in general, the content of lead in the root system of plants is higher than that in the stems, leaves and fruits of plants. The continuous accumulation of heavy metals in the soil will eventually lead to a decline in soil quality, thus affecting microbial activity, crop production and threatening ecosystem security and human health[13]The study of lead transport and transformation in the soil-plant system can reflect more realistically the many ecological problems left behind by the end of mining. Therefore, the study of the characteristics of lead transport and transformation in the soil-plant system can reflect more realistically the numerous ecological and environmental problems left behind in the mining area after the end of exploitation.

Yunnan, as a kingdom of non-ferrous metals, is rich in minerals, and the main minerals in an abandoned mining area located in southwestern Yunnan are lead and zinc ores, of which lead is a hazardous and toxic substance, and the enrichment effect of lead through the food chain will pose a serious threat to biodiversity and human health[14]。

2. The Content of the Study

2.1. An overview of the study area

The study area is located in an abandoned mining area in Pu'er, southwest Yunnan, with geographical coordinates of 101 ° 48 ′ 53 ″ E and 22 ° 29 ′ 17 ″ N. The abandoned mining area is characterized by complex structure, fold and fracture development, large topographic relief, high in the east and west and low in the middle. The highest peak in the territory, Laoqingliangzi, is located in the northeast of the territory, with an altitude of 2193m; The lowest point "Wulong Ferry" is located in the southwest of the country, with an altitude of 1400 meters. The abandoned mining area covers an area of about 12937 square meters, which is far from the urban area. The main mineral is lead-zinc ore, and its tailings are stacked in the open air. The four seasons in this region are mild, the temperature difference between the four seasons is not obvious, the perennial sunshine is sufficient, the climate is hot and humid, located in the Tropic of Cancer, and belongs to the subtropical climate. The annual average temperature is 18.3 ℃ - 22.1 ℃, the rainfall is abundant, the dry and wet seasons are distinct, and the annual average rainfall is 1345.4 mm. PH value of soil is generally neutral.

2.2. Sample collection and preparation

2.2.1. Sample collection

(1) Collection of soil samples from agricultural land

According to the requirements of the Code for Geochemical Evaluation of Land Quality (DB61/T 1401-2021), and based on data analysis and site survey, the plum blossom point distribution method is used to arrange the points[15]。 In this experiment, five sampling points were set up, taking the intersection point of two diagonals at four corners of agricultural land as the center point, and then taking the center point and four corners for five sampling points. A total of 15 soil samples of 0-20cm topsoil, 20-40cm middle soil and 40-60cm deep soil shall be collected for sampling, and bamboo chips shall be used for sampling. When one soil sample is collected, the soil on the bamboo slice used for sampling shall be removed before the next soil sample is collected.

(2) Collection of crop samples

The collection method of crop maize was implemented according to the requirements of land quality geochemical evaluation specification DZ/T0295-2016, and the sample sampling was carried out according to the layout of the soil sample site, five sampling points were selected, and sampling was carried out during the harvesting period of crop maize, and one sample of maize plant was randomly selected from each soil sample point, and the surrounding area of the sample point needed to be free of missing maize plants. The collected samples were put into sample bags, a total of five corn plants were taken, and the root, stem, leaf and fruit samples of each corn plant were sorted and packaged.

2.2.2. Sample pre-treatment

The soil samples were heated in an oven at 105-110 degrees Celsius until constant weight, and the difference in mass of the soil samples before and after drying was used to calculate the content of dry matter; the dried soil samples were then spread on a sample plate, and the soil samples were ground with a wooden stick and passed through a 100-purpose nylon sieve, and the samples were preserved in self-sealing bags. The samples were digested using an electric hot plate.

The samples were cleaned and the roots, stems, leaves and fruits of the maize plant were cut into 0.5-1 cm strips. The chopped plant samples were baked in an oven at 85-98 degrees Celsius for one hour, then the dried plant samples were placed in a mortar and pestle for grinding, and all the crushed plant samples were passed through a 20-purpose nylon sieve, and then finally put into self-sealing bags for preservation. The samples were digested by microwave digestion.

2.3. Determination of soil pH

Weigh 10 g of soil sample at each point, put them into 50 mL beakers respectively, add 25 mL of distilled water, put the beakers on the magnetic stirrer, mix for 2 minutes, and let stand for 30 minutes. First, calibrate the acid-base meter with standard buffer solution with pH value of 6.86, and then calibrate it with pH value of 4.01. Insert the pH meter electrode into the sample solution and record the pH value when the value is stable.

2.4. Determination of lead in soil on agricultural land

Soil samples from agricultural land were digested using an electric hot plate. Take 0.2 grams of soil samples into a crucible, add a small amount of distilled water to wet the soil samples and add 10 milliliters of nitric acid, add 9 milliliters of nitric acid when a small amount of heating is left with the electric hot plate, add 5 milliliters of hydrofluoric acid when there is no obvious particulate matter, and heat for 30 minutes, then add 1 milliliter of perchloric acid until the appearance of white smoke. Finally, 3 ml of nitric acid solution was added, and the sample was allowed to dissolve completely at low temperature, and then the sample was fixed in a 25 ml volumetric flask with nitric acid solution for the determination of the heavy metal lead by flame atomic absorption spectrophotometer. Three sets of parallel samples were made at the same time, and the average value was calculated as the heavy metal content of the samples[16]。

The roots, stems, leaves and fruits of maize plants were digested by microwave digestion. Firstly, 0.4 g each of the roots, stems, leaves and fruits of the maize plant samples were placed in the digestion jar, 8 ml of nitric acid was added, and the acid was driven on the acid drive rack for 1 h. The liquid was cooled down and then put into the microwave digestion apparatus, and the digestion was stopped until the liquid was cooled down, and then the gas in the digestion jar was opened slowly, and then acid was driven for 5 h. At the end of the digestion, the solution was fixed with distilled water to 40 ml, and the heavy metal lead was determined by a flame atomic absorption spectrophotometer. At the end of the digestion, the solution was diluted to 40 ml with distilled water, and then the determination of heavy metal lead was carried out by flame atomic absorption spectrophotometer. Three sets of parallel samples were taken at the same time, and the average value was calculated as the heavy metal content of the samples.

Blank samples were prepared without weighing the experimental samples, following the same experimental procedure.

3. Experimental Results and Analysis

3.1. Soil pH

Table 3-1. PH Value of Farmland Soil

Sample number	Soil sample 1	Soil sample 2	Soil sample 3	soil sample 4	soil sample 5	Mean
PH value	4.96	6.30	5.46	5.23	5.01	5.39

It can be seen from Table 3-1 that the average PH value of farmland soil in this study area is 5.39, and PH is less than 7, so the farmland soil is acidic.

3.2. Content of the heavy metal lead in soil samples, the

According to the detection, the average content of lead in topsoil soil at each point is 55.1, 194.1, 132.9, 151.5, 52.6 mg/kg, the average content of lead in middle soil soil is 51.8, 185.0, 82.6, 80.0, 51.9 mg/kg, and the average content of lead in deep soil soil is 50.8, 166.2, 80.5, 77.0, 50.8 mg/kg.

3.3. Levels of the heavy metal lead in crops

The heavy metal lead content in maize plants was mainly enriched in the root system and leaves, while the content of elemental lead in stems and fruits was zero. The

In this experiment, the content of lead in leaves and seeds of maize plants was determined to be zero. The possible reasons for this result are: first, the content of lead in stems and fruits was too low to reach the detection limit of the instrument, so the content of heavy metal lead was not measured; Second, it may be that the content of heavy metals in the sample was damaged by strong acid during the experiment, leading to experimental errors. Therefore, the experimental determination results show that the content of heavy metals in corn grains and samples is zero. There was a significant difference in lead content between roots, leaves, stems and fruits of maize plants, but there was no significant difference between stems and fruits.

3.4. Migration and transformation patterns of heavy metal lead in agricultural land

Soils in the study area showed a certain degree of enrichment of heavy metal Pb, and the enrichment capacity of agricultural soils for heavy metal Pb was as follows: surface soil>middle soil>deep soil.

The heavy metal lead in maize plants mainly accumulates in roots and leaves, and the content of lead in roots is higher than that in leaves. The limit index of corn listed in the national food safety standard is 0.4 mg/kg, while the content of heavy metal lead in corn fruit is zero, which does not exceed the national food safety standard. However, the content of roots and leaves of maize is higher than the limit index, which is polluted to a certain extent.

The distribution of Pb content in different parts of the maize plant was as follows: roots > leaves > stems and fruits. As a whole, different parts of the maize plant had different ability to transport heavy metals to the soil, with stronger ability in the root system and leaves, and weaker ability in the stems and kernels. The process of heavy metal migration from agricultural soil to roots, stems, leaves and fruits of corn plants is extremely complicated, and the heavy metal lead content measured in this study was affected by the source, and generally tended to decrease with the decline of the soil layer; with the increase of the heavy metal lead content in the soil, the heavy metal lead migrated along with the root system of the corn plants and was enriched in the roots and leaves of the plants.

The results of the experimental study showed that the heavy metal content in maize plants was correlated with the heavy metal content in the soil of the agricultural land, when the heavy metal content in the soil increased, the heavy metal content in maize plants would also increase, on the contrary, when the heavy metal content in the soil was reduced, the heavy metal content in maize plants decreased; and then comparing the content of the heavy metal Pb in maize plants in the five points, it could be obtained that the heavy metal Pb The migration capacity of heavy metal lead in maize plants at five locations was compared: root system > leaf > stem and fruit.

4. Conclusion

This experiment was conducted to determine the heavy metal lead content in different parts of agricultural soils and maize plants, and to investigate the migration pattern of heavy metals in soils and maize plants. We chose to analyze the migration and transformation patterns of heavy metal lead in the soil by focusing on the element lead and using the topsoil, middle soil, deep soil of the agricultural land soil and the roots, leaves, stems, and fruits of the maize plants as the research objects, and we drew the following conclusions based on the present study.

(1) Agricultural soils in the study area have a certain degree of enrichment of heavy metal Pb, and the enrichment capacity is generally manifested as surface soil>middle soil>deep soil.

(2) The data obtained from the determination of Pb in maize plants showed that the content of heavy metal Pb in maize plants increased with the increase of the concentration of heavy metals in the soil of the agricultural land, and the heavy metal Pb in the soil reached the effect of migration through the root system of maize plants, and the higher the concentration of heavy metals in the soil, the higher the capacity of the maize plants to migrate the heavy metal Pb.

(3) The distribution of lead in the roots, stems, leaves and fruits of maize plants is characterized by the fact that the content of lead is higher in the roots and leaves than in the stems and fruits, and that it accumulates in the roots and leaves over a long period of time. Maize plants are more capable of transporting Pb in the roots and leaves and less capable of transporting Pb in the stems and kernels, but there is a potential for heavy metals to be transported from the soil to the edible parts of the plant.

(4) The enrichment capacity of maize plants for Pb was in the following order: roots > leaves > stems and fruits, and the

roots and leaves of maize plants were contaminated with heavy metal Pb to a certain extent. The transport capacity of heavy metal Pb in the soil-corn plant system was as follows: roots > leaves > stems and fruits.

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