Heavy Metals Pollution in Soil Around the Lead-zinc Smelting Plant in guanzhong Plain

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Abstract: [Objective] T To analyze and determine the content of eight heavy metals Cd, Cr, Cu, Pb, Hg, Zn, As, and Ni in 40 soil samples collected around a lead-zinc smelting plant in Guanzhong through experimental analysis, and to preliminarily grasp the content of heavy metals in the soil around the smelting plant, and to conduct pollution research and evaluation.. [Method] In mid to late April 2020, 40 soil samples (with a sampling depth of 0-30 cm) were collected from the vicinity of a lead zinc smelter in Guanzhong. The heavy metal content was determined through transcoding, natural air drying, and grinding processes.. [Results] The average contents of Cd, Cr, Cu, Pb, Hg, Zn, As, and Ni in the soil around a lead zinc smelter in Guanzhong were 0.40, 85, 26.0, 48, 0.078, 108, 12.5, and 26 mg · kg-1, respectively. Except for Ni, the average contents of Cd, Cr, Cu, Pb, Hg, Zn, and As were higher than the background values of soil elements in China and Shaanxi Province, especially Cd, Hg, and Pb, The content is 4.26, 2.60, and 2.28 times the background values of soil elements in Shaanxi Province, and 4.12, 1.2, and 1.85 times the background values of soil elements in China. By calculating the standard deviation and coefficient of variation, it was found that the standard deviation and coefficient of variation of Cd, Pb, and Zn in the soil around the smelter were relatively large, indicating that these three heavy metal elements accumulated significantly in the soil.. [Conclusion] The soil around a lead-zinc smelter in Guanzhong is mainly contaminated by multiple heavy metal complexes, mainly Cd pollution. The atmospheric sedimentation around the smelter and dust from mining sites may be the main sources of pollution..

Keywords: lead-zinc smelting plant area; Soil; Heavy metals; Pollution assessment.

1. Introduction

Soil not only provides permanent habitat for human beings, animals and plants, but also provides a beautiful home for all things in the world. Because of this, the soil almost bears 90% of all kinds of pollutants from nature. The "three wastes" generated by various production activities, namely waste water, waste gas, waste residue, etc., will pollute the soil, and the pollution caused by heavy metals is the most serious [1]. Heavy metal pollution in soil refers to the phenomenon that the content of heavy metal elements in soil increases due to human activities, including trace pollution exceeding the background value and excessive pollution caused by long-term accumulation and migration [2]. Heavy metals can interact strongly with proteins and other enzymes in the human body to inactivate them, and they are easy to remain and accumulate, and cannot be biodegraded, causing irreversible damage to the human body and soil. Therefore, heavy metal pollution has become an important factor threatening human health and ecosystem . Therefore, it is urgent to solve this problem [3-4].

Research shows that the sources of soil heavy metal pollution are mainly divided into two aspects. The first is natural sources, such as weathering of soil forming parent material, chemical migration caused by hydraulic and wind transport, and the second is human interference, such as metallurgy, mining, pesticide application, transportation, etc. [5]. Compared with these two aspects, the latter has a greater impact, especially metallurgy and mining. The "three wastes" generated in the process of metallurgical and mining production, as well as a large number of heavy metal elements in dust and tailings, will cause serious pollution to the surrounding soil [6].

In recent years, heavy metal pollution incidents in soil at home and abroad have occurred frequently, which has attracted great attention. Heavy metal pollution in soil of smelting plant has also become a current research hotspot [7-11]. Therefore, in the middle and late April of 2020, this study collected, analyzed and tested the content of

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heavy metals in the soil around a lead-zinc smelter in Guanzhong area, and evaluated the pollution status, in order to find the source of heavy metal pollution in the soil in this area, and provide a strong basis for the protection and treatment of heavy metals in the future..

2. Materials and methods

2.1 Overview of the study area

Changqing Town, Baoji City, is low in the middle and high in the east and west, belonging to a semi-arid and semi-humid monsoon climate, with an annual average temperature of 11.5℃and annual rainfall of 600-700 mm. In August 2009, the social event of "children's blood lead exceeding the standard" in Changqing Town caused heated discussion among people from all walks of life. This study took the soil around a lead-zinc smelter in the town as the object to analyze and determine the content of heavy metal elements in the soil.

2.2 Sample collection

In late April 2020, according to the actual investigation on the site, the topography and land use types of the smelter area, the sampling points are mainly distributed in the southeast and northwest directions of the smelter. Because the soil characteristics around the smelter are similar and the land use functions are the same, the "systematic random distribution method" is used to arrange the soil sampling points in this study. 20 soil sampling points are arranged in these two directions, and 40 soil sampling points are arranged in total. Four soil samples (sampling depth of 0-30 cm) were collected at each sampling point. After being fully mixed, about 1 kg of soil samples were retained by the "quartering method" and placed in self sealing bags to prevent the collected samples from being polluted by the outside world. Finally, 40 soil samples were collected in the southeast and northwest directions of the smelter.

The collected soil samples shall be brought back to the laboratory as soon as possible for unified transcoding, and then placed in a ventilated and dark environment at room temperature to dry naturally. The dried soil samples were grinded and passed through 2 mm, 1 mm and 0.149 mm nylon sieves and divided into three parts. One is used to determine the basic physical and chemical properties of soil, the other is used to determine the content of heavy metal elements Cd, Cr, Cu, Pb, Hg, Zn, as and Ni, and the other is reserved for preservation.

2.3 Sample handling and testing

The soil sample treatment and test methods are shown in Table 1 below.

In the process of testing the content of heavy metals in soil samples, Gss-34 (national standard soil sample) was inserted for quality control. All the reagents used in this study were analytically pure, and all samples were blank with corresponding reagents. The determination of parallel samples reached 20%.

The repeatability of the analysis results was evaluated by calculating the relative deviation (RD) of the test results of parallel samples. The relative deviation (RD) is calculated by the following formula:

$$RD = \frac{R_1 - R_2}{R_1 + R_2}$$

Where R_1 represents the result of R sample and R_2 represents the result of parallel samples of R. According to the statistical results, the relative deviation of all detected parallel samples is within the scope of quality control.

Table 1 Items and methods of soil nutrient determination

Items	Methods	Standard
pH	Acidity meter method	NY/T 1377-2007
organic matter	Potassium dichromate external heating method	LY/T 1237-1999
Hg	Atomic fluorescence spectrophotometry	GB/T 22105.1-2008
As		GB/T 22105.2-2008
Cd、Cr、Cu、Pb、Zn、Ni	ICP-MS	HJ 803-2016

2.4 Evaluation method of heavy metal content in soil

The geoaccumulation pollution index method can comprehensively reflect the pollution degree of heavy metal elements in soil. Other pollution assessment methods only consider human interference factors and background values of heavy metal elements in soil, while natural sources, such as changes in background values caused by diagenesis, are often ignored. The geoaccumulation pollution index law fully takes this factor into account and makes up for the shortcomings of other evaluation methods. Therefore, the method of geoaccumulation pollution index is used for evaluation in this experiment.

The geoaccumulation pollution index method was proposed by the German scientist m ü ller in the late 1960s to evaluate the pollution degree of heavy metals in solid sediments and other substances. The geoaccumulation pollution index method is an index for quantitative study of heavy metal pollution in water sediments [12], which has been widely used in the study of soil heavy metal pollution. The specific calculation formula is as follows:

$$I_{geo} = \log_2[C_i/(k \times B_i)]$$

Where: I_{geo} —geoaccumulation pollution index

C_i—actual measured concentration of heavy metal element I in soil

B_i—background value of soil heavy metal element i

k—constant, correction for the change of background value caused by diagenesis (generally 1.5)

3. Results and discussion

3.1 Content of heavy metal elements

Through analysis and measurement, it was found that the soil around a lead zinc smelting plant in Guanzhong is slightly alkaline, with a pH range of 7.65-8.68 and an average value of 8.24. The soil organic matter content is 12.5-58.0 g·kg^{-1}, with an average value of 27.9 g·kg^{-1}.
The content range of heavy metal elements Cd, Cr, Cu, Pb, Hg, Zn, As and Ni in the soil around the smelter is 0.11-0.61 mg·kg^{-1}, 50-135 mg·kg^{-1}, 15.4-34.9 mg·kg^{-1}, 22-77 mg·kg^{-1}, 0.042-0.128 mg·kg^{-1}, 6.6-15.8 mg·kg^{-1}, 70-152 mg·kg^{-1}, and 20-34 mg·kg^{-1}, respectively, with an average content of 0.41, 86, 25.9, 47, 0.077, 106, 12.7, and 24 mg·kg^{-1}. Among the eight heavy metal elements, except Ni, The average content of other heavy metals is higher than the background value of soil elements in China and Shaanxi Province, especially Cd and Pb, which are 4.26 and 2.27 times of the background value of soil elements in Shaanxi Province, 4.10 and 1.84 times of the background value of soil elements in China. According to the above table, the standard deviation and coefficient of variation of heavy metal elements Cd, Pb and Zn in the soil around the smelter are large, indicating that their accumulation in the soil is obvious. To sum up, the eight heavy metal elements measured in this study have been polluted and accumulated in different degrees in the soil of the region.

Table 2 Heavy Metal Content in the Soil Around a Lead Zinc Smelter in Guanzhong

heavy metal	Maximum value	Minimum value	Average value
Cd	0.61	0.11	0.41
Cr	135	50	86
Cu	34.9	15.4	25.9
Pb	77	22	47
Hg	0.128	0.042	0.077
Zn	152	70	106
As	15.8	6.6	12.7
Ni	34	20	24

3.2 Enrichment characteristics of heavy metal elements

The results of heavy metal pollution in the soil around the lead-zinc smelter based on the cumulative pollution index method are shown in Table 3 below. From the average value, the soil in the study area is only polluted by CD, Pb and Hg, and the pollution of other heavy metals is not reflected. However, from the maximum value, CD has reached a moderate to strong pollution level in some areas, Pb and Hg have reached a moderate pollution level, and Zn, Cu and CR have reached a mild to moderate pollution level. From the sampling area, the soil in the northwest is more polluted by heavy metals than that in the southeast. Among them, CD and Pb pollution is the most serious, and has reached the moderate to strong pollution level. According to the analysis, this phenomenon is most likely related to the local wind direction. The local wind direction is mainly northwest wind, which leads to the dust, dust and Aerosol and other pollutants have chemical migration in the process of wind transport. Therefore, the soil in the northwest is seriously polluted by heavy metals. In addition, the soil beside the highway is polluted by the tail gas emitted by various vehicles, resulting in the high content of Pb and Hg elements. In general, the pollution of Pb, CD and Hg in the soil around a lead-zinc smelter in Guanzhong is serious.

3.3 Variation characteristics of heavy metal elements with distance

There are a lot of heavy metal elements in the smoke and dust discharged from lead-zinc smelters. With the settlement and diffusion of these smoke and dust, heavy metal elements will gradually be enriched in the surrounding soil environment. After smoke, dust and other pollutants enter the atmosphere, the degree of soil pollution varies with the distance from the pollution source and the location. The most likely reason for this phenomenon is that natural environment, geography, monsoon and other conditions can affect the formation of microclimate in different regions, and then affect the migration direction of pollutants. It is understood that in regions with different longitudes and latitudes, altitudes, landforms and other conditions, the climatic conditions are different, and the pollution degree and mode of pollutants such as soot and dust in the atmosphere to the surrounding environment are also different. In this experiment, the topsoil 0-1500 m away from the northwest of a lead-zinc smelter in Guanzhong was collected, and the contents of CD, Hg and Pb were determined and analyzed. Finally, the horizontal distribution of the contents of these three heavy metals was obtained.
The specific method of collecting soil samples in this experiment is as follows: take a sample every 50 m at a distance of 0-400 m from the northwest of a lead-zinc smelter in Guanzhong, and take a sample every 100 m at a distance of 400-1500 m, a total of 20 soil samples are collected. Finally, it was found that the content of heavy metal elements Cd, Hg and Pb in the soil in the northwest of a lead-zinc smelter in Guanzhong decreased with the increase of the distance from the smelter. The closer the distance from the lead-zinc smelter, the higher the content of heavy metal elements in the soil, that is, the more serious the heavy metal pollution. It can be seen from the figure that within the range of 0-400 m from the smelter, the slope of the change curve of CD, Hg and Pb content is large, indicating that the content of heavy metal elements changes greatly and decreases rapidly, that is, the attenuation is sharp, while within the range of 400-1500 m from the smelter, the change curve of CD, Hg and Pb content is close to the level, that is, the change of heavy metal element content is significantly slowed down, and the attenuation trend is significantly weakened, so it can

be inferred that, The smelter is an important pollution source that leads to high content of heavy metal elements in the soil in this area. To sum up, the contents of heavy metal elements Cd, Pb and Cu in the soil around a lead-zinc smelter in Guanzhong decreased with the increase of the distance from the pollution source, and the attenuation of the content of heavy metal elements had obvious stages.

4. Conclusion

(1) The average contents of CD, Cr, Cu, Pb, Hg, Zn, as and Ni in the soil around a lead-zinc smelter in Guanzhong were0.41, 86, 25.9, 47, 0.077, 106, 12.7, and 24 $mg\cdot kg^{-1}$, respectively. Except for Ni, the average contents of CD, Cr, Cu, Pb, Hg, Zn and as were higher than the background values of soil elements in China[13] and Shaanxi Province, especially Pb and CD, which were 2.27 and 4.26 times higher than the background values of soil elements in Shaanxi Province, respectively, They are 1.84 and 4.10 times of the background values of soil elements in China, respectively. Compared with the background value, the order of the contents of eight heavy metals from high to low was cd>hg>pb>zn>cr>cu>as>ni.
(2) The evaluation results of geoaccumulation pollution index show that, from the average value, the soil around the smelter is only polluted by CD, Pb and Hg, and the pollution of other heavy metals is not reflected. However, from the maximum value, CD has reached a moderate to strong pollution level in some areas, Pb and Hg have reached a moderate pollution level, and Zn, Cu and CR have reached a mild to moderate pollution level.
(3) The analysis of the variation characteristics of heavy metal elements with distance shows that the contents of heavy metal elements Cd, Pb and Cu in the soil around the smelter decrease with the increase of distance from the pollution source, and the attenuation of heavy metal elements has obvious stages.
To sum up, the soil around a lead-zinc smelter in Guanzhong is mainly polluted by a variety of heavy metals, mainly CD. The atmospheric deposition and diffusion around the smelter, as well as the smoke and aerosol emissions, may be the main pollution sources.

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