Speciation characteristics of heavy metals in soil around typical coal gangue hills in fengfeng mining area

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Abstract: The purpose of study was to discuss the influence of coal gangue on soil environmental quality, the speciation content of heavy metals in soils around coal gangue hills was analyzed. The results showed that: firstly, the residual state of each heavy metal accounted for most of the total amount, and the exchangeable state content (except As) was the smallest. Secondly, in the surface soil (0-20cm) of downwind around typical coal gangue hills, the contents of exchangeable and carbonate binding states in Cu, Hg and Cr were relatively large, which were 2.14mg kg⁻¹, 1.13mg kg⁻¹, 1.79mg kg⁻¹; 1.88mg kg⁻¹, 1.19mg kg⁻¹, 1.52mg kg⁻¹, respectively. It showed great potential ecological harm. The content of Fe-Mn oxides bound in Pb was higher, which was 9.35mg kg⁻¹. The content of bound to organic in Cr, Cu and Hg was higher, which were 13.67mg kg⁻¹, 12.52mg kg⁻¹, 10.18mg kg⁻¹, respectively. Thirdly, the activity coefficient and migration coefficient of Cu in the soil in the study area were relatively large. It showed strong bioavailability and posed the greatest potential harm to the environment. In the surface soil (0-20cm) of downwind, average effectiveness of Hg reached 10.96%, and the maximum value was 13.84%. It showed strong biological activity and instability.

1. Introduction

The Fengfeng mining area is located in Handan City, Hebei Province. The region is a warm temperate semi-humid continental monsoon climate. The annual average temperature is 14.1°C, and the annual average precipitation is 627mm. The west side of Fengfeng mining area is intermountain basin, and the east side of Fengfeng mining area is inclined plain, the highest elevation is 891 meters. The vegetations of the area mainly include artificial agricultural vegetation and semi-artificial woodland-shrub and shrub grassland. The mining area has a long history of coal mining. Due to the unreasonable mining of the mining area and the promulgation of national policies, the small and medium-sized coal mines have been basically closed. But it also left a lot of environmental problems. For example, a large amount of coal gangue is stored in the mining area. In the long-term storage, it is easy to occur spontaneous combustion and dust, causing serious pollution to the atmosphere, water and soil[1]. In this paper, the surrounding soil of coal gangue hill in Fengfeng mining area was taken as the research object, the tessier five-step extraction method[2] was used to determine the speciation of heavy metals, through the analysis of the characteristics of morphological content and migration characteristics, it provides a scientific basis for soil pollution prevention and environmental precision management in mining areas.
2. Materials and methods

2.1 Sample collection
Considering the factors of landform and wind direction, the experiments took the coal gangue hill as the center. The directions of two sampling lines were downwind (southeast) and upwind (northwest) directions in this research. Each sampling line was designed with 10 sampling points, which are 0m, 20m, 40m, 60m, 80m, 100m, 150m, 200m, 300m and 400m. Two depths of soil were collected at each sampling site, including surface soil (0-20cm) and deep soil (20-40cm). Each sample was about 5kg, and there were 40 soil samples in total. Three parallel sampling points were selected from each sampling point, and multi-point mixed sampling was used to collect soil samples. The soil samples collected were quartered into a sample bag and numbered. After removing impurities, the soil samples were naturally air-dried, grind through 200 mesh screen, then it was used for the determination and analysis of heavy metal speciation content in soil.

2.2 Determination method
Based on the previous investigation and analysis, five heavy metals (Cu, Hg, Cr, As and Pb) were selected. The Tessier five-step extraction method procedure is as follows, the quantitative sample is weighed, Water, magnesium chloride, sodium acetate, sodium pyrophosphate, hydroxylamine hydrochloride and hydrogen peroxide were used as extraction agents, it extracts exchangeable states; Carbonate binding state; Iron (manganese) oxide binding state; Organic bound state; Residual state, preparation of various forms of analysis liquid. First, the residue after appropriate amount of the above morphological analysis solution was taken, and then the residue state analysis solution was prepared after being treated with hydrochloric acid, nitric acid, perchloric acid and hydrofluoric acid[3]. The speciation content of heavy metal (Cu, Cr, Pb) in soil samples were determined by ICP-OES, The speciation content of heavy metal (Hg, As) in soil samples were determined by Atomic fluorescence spectrometry.

3. Results

3.1 Speciation characteristics of heavy metals in soils
Determination of five forms of heavy metals in soil around coal gangue in Fengfeng mining area by Tessier continuous extraction method, and they were exchangeable (F1), Carbonate binding state (F2), Fe-Mn oxides bound (F3), Organic binding state (F4), Residual state (F5), respectively. The results are shown in Table 1.

| Speciation | downwind (southeast) mg kg⁻¹ | upwind (northwest) mg kg⁻¹ |
|------------|-----------------------------|-----------------------------|
|            | surface soil (0-20cm) | deep soil (20-40cm) | surface soil (0-20cm) | deep soil (20-40cm) |
| Cu         |                      |                           |                          |
| F1         | 1.13                 | 0.65                      | 0.61                     | 0.26                     |
| F2         | 1.88                 | 1.74                      | 0.95                     | 0.75                     |
| F3         | 5.80                 | 3.46                      | 2.61                     | 1.56                     |
| F4         | 12.52                | 12.22                     | 6.99                     | 6.48                     |
| F5         | 15.53                | 16.87                     | 9.72                     | 10.39                    |
| Hg         |                      |                           |                          |
| F1         | 1.79                 | 0.84                      | 0.37                     | 0.18                     |
| F2         | 1.19                 | 0.81                      | 0.57                     | 0.31                     |
| F3         | 3.42                 | 2.71                      | 1.90                     | 1.17                     |
| F4         | 10.18                | 8.86                      | 4.06                     | 3.19                     |
| F5         | 16.50                | 17.68                     | 8.05                     | 8.36                     |
| Cr         |                      |                           |                          |
| F1         | 2.14                 | 0.96                      | 0.52                     | 0.25                     |
| F2         | 1.52                 | 1.00                      | 0.94                     | 0.56                     |
| F3         | 4.15                 | 3.22                      | 3.07                     | 1.87                     |
| F4         | 13.67                | 11.37                     | 7.70                     | 6.10                     |
As F1 / / / / F2 0.30 0.18 0.10 0.85
F3 1.21 0.84 0.57 0.40
F4 0.93 0.33 0.41 0.20
F5 7.83 7.08 5.21 4.93

Pb F1 0.65 0.42 0.27 0.21
F2 / / / /
F3 9.35 8.38 6.53 5.53
F4 3.89 2.88 2.12 1.62
F5 11.22 11.89 8.65 10.22

Note: The sign (/) indicates that the detection limit of the instrument has not been reached.

(1) Downwind
In the surface soil (0-20cm), the contents of exchangeable heavy metals (except As) were the smallest. The contents of Cu, Hg and Cr are relatively large, they were 2.14mg kg$^{-1}$, 1.13mg kg$^{-1}$ and 1.79mg kg$^{-1}$, respectively. The content of five heavy metal elements in carbonate were small, and the content of Cr, Cu and Hg were relatively large. They were 1.52mg kg$^{-1}$, 1.88mg kg$^{-1}$ and 1.19mg kg$^{-1}$, respectively. Cr, Cu and Hg showed great potential ecological harm. The exchangeable content of As and the carbonate binding content of Pb did not reach the detection limit of the instrument. The results showed that the content of these two species was not high, their properties were stable and their ecological effects were small.

Among the five heavy metals, the highest content of Fe- Mn oxide is Pb, which is 9.35mg kg$^{-1}$. The reason may be that Pb can be tightly adsorbed on the surface of Fe- Mn oxides, resulting in a high content of Fe- Mn oxide binding state. Cr, Cu and Hg all have high Fe- Mn oxide binding content, which was 4.15mg kg$^{-1}$, 5.80mg kg$^{-1}$ and 1.19mg kg$^{-1}$, respectively. The content of strong organic binding states of Cr, Cu and Hg were relatively high, they were 13.67mg kg$^{-1}$, 12.52mg kg$^{-1}$ and 10.18mg kg$^{-1}$, respectively. It showed that Cr, Cu and Hg were more likely to form highly stable organic compounds. The strong organic binding state was formed by the outer layers of organic and mineral particles chelate with heavy metals in the soil, indicating that it was not dangerous to dissolve in water. It showed that it was insoluble in water and not dangerous.

The content of residual state was the largest among all the forms of heavy metals. The content of Cr residue is the largest, which is 22.64mg kg$^{-1}$. The content of As residue is the smallest, which is 7.83mg kg$^{-1}$. The high proportion of soil residue in the study area may be related to pH. The soil in the study area belongs to alkaline, and alkaline environment is conducive to the transformation of heavy metals from exchangeable state to residual state.

In the deep soil, the content of exchangeable state of heavy metals (except As) is the smallest. The exchangeable state content of Cr is the largest, which is 0.96mg kg$^{-1}$. The content of carbonate binding state of five heavy metal elements is small. The content of Cu in carbonate bound state is the largest, which is 1.74mg kg$^{-1}$, and Cu shows great potential ecological harm.

(2) Upwind
In the surface soil (0-20cm), the content of exchangeable state of heavy metals (except As) is the smallest. The exchangeable state content of Cr is the largest, which is 0.61mg kg$^{-1}$. The content of Cu and Cr in carbonate is large, which are 0.95mg kg$^{-1}$ and 0.94mg kg$^{-1}$, respectively. In the deep soil (20-0cm), the content of exchangeable state of heavy metals (except As) is the smallest. The contents of exchangeable states of Cu and Cr are large, which are 0.26mg kg$^{-1}$ and 0.25mg kg$^{-1}$, respectively. The content of carbonate binding state of five heavy metals is small. The content of carbonate binding state of As is the largest, which is 0.85mg kg$^{-1}$.

(3) Vertical distribution of heavy metal speciation
In the downwind and upwind directions, the ratio of exchangeable and carbonate-bound heavy metals in surface soil (0-20cm) is higher than that in deep soil (20-40cm). A large number of heavy metals were discharged into the soil from coal gangue mountain through spontaneous combustion weathering. The study area was weakly alkaline, which will increased the negative charge of the
surface soil, enhanced the adsorption, reduced the migration of heavy metals in the soil, and made heavy metals concentrated in the surface soil.

3.2 Bioavailability analysis in soil around coal gangue

The bioavailability of heavy metals is the ratio of the sum of exchangeable and carbonate-bound states to total. Bioavailability is the process of analyzing the migration, transformation and bioaccumulation of heavy metals in the environment [4]. The bioavailability of heavy metals is shown in Figure 1.

With the increase of the distance from coal gangue mountain, the proportion of soil heavy metal availability basically showed a downward trend. The activity coefficient and migration coefficient of Cu in the soil of the study area were relatively large. It showed strong bioavailability and posed the greatest potential harm to the environment. In the surface soil (0-20cm) of downwind, the validity of Hg average value was 10.96%, and the maximum value was 13.84%. It showed strong biological activity and instability. Other heavy metal elements in the study area were less effective and posed less potential harm to the environment. The distribution of heavy metal speciation in soil was affected by pollution, soil physical and chemical properties, meteorological conditions and other factors. The content of available heavy metals in soil was negatively correlated with clay content, cation exchange capacity and pH, it was positively correlated with organic matter. The bioavailability of heavy metals decreased with the increase of clay content, and the availability of heavy metals decreased with the increase of cation exchange capacity in soil. This is because the increase of cation exchange capacity will lead to the increase of soil adsorption and fixation of heavy metal ions, which reduces bioavailability of heavy metal [5].

4. Conclusions

(1) The results of morphological analysis: the residual state of each heavy metal accounted for most of the total amount, and the exchangeable state content (except As) was the smallest. It was not easy for plants to absorb heavy metals. In the surface soil (0-20cm) of downwind around typical coal gangue hills, the contents of exchangeable and carbonate binding states in Cu, Hg and Cr were relatively large, which were $2.14 \text{mg kg}^{-1}, 1.13 \text{mg kg}^{-1}, 1.79 \text{mg kg}^{-1}$; $1.88 \text{mg kg}^{-1}, 1.19 \text{mg kg}^{-1}, 1.52 \text{mg kg}^{-1}$, respectively. It showed greater potential ecological harm. The content of Fe-Mn oxides bound in Pb was higher, which was $9.35 \text{mg kg}^{-1}$. The reason may be that Pb can be tightly adsorbed on the surface of iron, manganese and other oxides, resulting in high content of iron-manganese oxide bound state. The
content of bound to organic in Cr, Cu and Hg was higher, which were 13.67mg kg$^{-1}$, 12.52mg kg$^{-1}$, 10.18mg kg$^{-1}$. It shows that Cr, Cu and Hg are more likely to form highly stable organic compounds.

(2) In the downwind and upwind directions, the ratio of exchangeable and carbonate-bound heavy metals in topsoil (0-20cm) is higher than that in deep soil (20-40cm). The study area was weakly alkaline, which increased the negative charge of the surface soil, enhanced the adsorption and enriched the heavy metals in the surface soil.

(3) The activity coefficient and migration coefficient of Cu in the soil in the study area were relatively large. It showed strong bioavailability and posed the greatest potential harm to the environment. In the surface soil (0-20cm) of downwind, the validity of Hg average value was 10.96%, and the maximum value was 13.84%. It showed strong biological activity and instability.

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