Distribution of heavy metals and pollution evaluation in soil surrounding the metal mining area

Aiming at the problem of heavy metal pollution in soil surrounding the metal mining area, the heavy metal pollution is evaluated and studied from 4 aspects, including the surface soil around the metal mining area, the soil profile, the different directions of the mining area and the morphological characteristics of heavy metals in the surface soil. The results show that the pollution level of Cd and Pb elements is the highest in the soil, which are classified as severe pollution and moderate pollution respectively. The pollution level of Cu, Zn, As and Ni belongs to light pollution, and the pollution level of Cr and Hg is the lowest. The calculation results of the cumulative index weighted values in the soil shows that the soil pollution around the metal mining area is more serious, with the pollution in most areas seriously exceeding the standard. Heavy metals are mostly concentrated within a range of 10cm of surface soil. With the increase of depth, the content of heavy metals decreases rapidly. When the depth exceeds 1m, the soil is basically clear of heavy metal pollution. The content of heavy metals in the west and south of the metal mines is higher than that in the east and the north. Cu, Ni, Pb, Zn and Cr are mainly in the residual form, accounting for 65.4% of the overall form, followed by the oxidation form with an average value of 19.6%, then followed by reducible form, with an average value of 9.2%, and the proportion of exchangeable form is the lowest, accounting for 6.4%. The average sum values of the residual and exchangeable forms of these 5 elements can reach to more than 70%, thus they are easy to adsorb onto plants or humus and other objects on the surface soil, causing serious damage to the surrounding environment.

Keywords: Soil, heavy metal pollution, profile, morphological mnalysis, metal mining area.

1. Introduction

Which the rapid development of China's economy, the demand for all kinds of heavy metals is also increasing. With a long mining cycle, a large mining area and other characteristics, metal mining will inevitably lead to serious pollution to the surrounding soil, crops, rivers and the like, due to gale, migration and infiltration with different kinds of heavy metal elements, thus causing damage to the ecological environment and threatening human health [1-4].

Soil is the first acceptor of heavy metals. Thus it is necessary to study the problem of heavy metal pollution in soil around the mining area, its distribution characteristics and migration and infiltration under different environmental media, because of the long incubation period, difficulty in degradation, easy absorption by plants and crops causing secondary pollution and other characteristics of heavy metal elements. Scholars from various countries have also gained considerable achievements, which mostly focus on the spatial distribution, pollution evaluation, source identification and morphological analysis of heavy metals [5-10]. Hongxia et al., (2014) used DOM algorithms to study the distribution of coal gangue of coal mine in the soil and its influence on the surrounding ecological environment [11]; Timofeev evaluated the distribution of heavy metals in the surrounding soil of the mining area, based on the pollution load index method [12]; Ullrich and Sterckeman's research showed that the content of heavy metals decreased significantly with the depth of soil, and the heavy metal species in soil were related to heavy metal migration and pollution time. The migration and infiltration rate of heavy metals in soil are far lower than its immigration rate into soil [13-14]. Liu et al., (2013) analyzed the soil composition around the non-ferrous metal mining area and found that the closer to the mining area and the metal smelter, the higher the pollution of the surface soil is [15]; Rodríguez et al. used the environmental risk index method and the cumulative index method to separate Pb, Zn, Cd and Cu elements commonly found in the soil around the mining area. The results showed that the content of heavy metals in the soil seriously exceeded the standard [16].

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Aiming at the heavy metal pollution problem in soil surrounding the metal mining area, heavy metal pollution is evaluated and studied in the present paper from 4 aspects, including the surface soil around the metal mining area, the soil profile, the different directions of the mining area and the morphological characteristics of heavy metals in the surface soil, with single factor pollution index method, comprehensive evaluation index method and cumulative index algorithm. The results will provide the direction and basis for the governance of heavy metal pollution in mining areas.

2. Test materials and research methods

2.1 SAMPLE COLLECTION AND PREPARATION

With one metal mine as research background, a total of 50 sampling points of the surface soil and profile soil surrounding the metal mining area were selected and 5 soil samples were collected within 30 meters range with each point as the center. The mean value of heavy metal content detection for 5 samples was taken as the mean value of each sampling point. Samples selected at the site were stored in sealed bags, and then put in the laboratory for later use after natural air-drying, grinding and screening.

The test of soil heavy metal content mainly includes the determination of pH value and detection of the content of 8 heavy metals such as Cu, Pb, Zn, Cd, Cr, As, Ni and Hg. The soil samples were dissolved in high temperature with nitric acid perchloric acid. The contents of Cu, Zn and Ni in soil were determined by flame atomic spectrometry, Cd, Pb and Cr measured by graphite furnace yard spectrometer and Hg and As detected by fluorescence detector, BCR sequence extraction was used to analyze the morphological characteristics of heavy metals in surface soil. The later data processing was mainly based on Matlab, Origin and SPSS software.

2.2 DATA CALCULATION

In general, the single factor pollution index P_i and the comprehensive evaluation index P_c were used to evaluate the pollution degree of heavy metals in the soil:

$$P_i = M V_i / S_t \qquad \dots \qquad (1)$$

$$P_{c} = \sqrt{\frac{(MV_{i}/S_{i})_{mean}^{2} + (MV_{i}/S_{i})_{max}^{2}}{2}} \qquad \dots \qquad (2)$$

In the formula, MV_i is the measured value of the single heavy metal pollution index, S_i the standard value of the heavy metal pollution index, $(MV_i/S_i)^2_{mean}$ the mean value of single factor pollution index and $(MV_i/S_i)^2_{max}$ the corresponding maximal value. Table 1 shows the evaluation rating of the comprehensive evaluation index P_c of soil heavy metal pollution.

Cumulative index I_{geo} is used to evaluate the cumulative pollution degree of heavy metals in soil surrounding the mine area.

$$I_{geo} = \log_2 \frac{MV_i}{1.5S_i} \qquad ... \qquad (3)$$

The weighted value of the cumulative index can be used to evaluate the overall pollution of the soil around the metal mining area. Table 2 shows grading indicator of cumulative index of the heavy metal in soil.

3. Test results and discussion

3.1 Evaluation of surface soil pollution around the mining area

The surface soil around metallogenic mines is the direct acceptor of heavy metal pollution, and crops, plants and water sources are in direct contact with the surface soil. Therefore, it is of great practical significance to study the heavy metal pollution degree of surface soil. Table 3 shows the overall pollution of heavy metals at 50 sampling points in the soil around the metal mine. The calculation results of P_i and P_c are as follows. It can be seen from the table that the P_i and P_c values of Cd and Pb in soil are the highest in all heavy metals, with the mean P_i values of 6.17 and 2.36 respectively, and the mean P_c values reaching 10.62 and 2.95 respectively, thus they are rated as severe and moderate pollution. The P_c values of Cr and Hg are less than 0.7, indicating that the surface soil in the study area is not polluted by them. The P_c values of Cu, Zn, As and Ni are between (0.7, 2), indicating that the soil in the study area is slightly polluted by them. The pollution

TABLE 1: COMPOSITE EVALUATION INDEX OF SOIL HEAVY METAL POLLUTION DEGREE $0.7 < P_c \le 1$ Calculated value $P_c \leq 0.7$ $1 < P_c \le 2$ $2 < P_c \leq 3$ $P_c > 3$ Level 1 2 3 4 Pollution degree Normal Warning Slight pollution Moderate pollution Heavy pollution

TABLE 2: CUMULATIVE INDEX OF SOIL HEAVY METAL POLLUTION DEGREE									
Calculated value	$I_{geo} < 1$	$1 \le I_{geo} < 2$	$2 \le I_{geo} < 3$	$3 \le I_{geo} < 4$	$4 \le I_{geo} < 5$	5 <igeo< th=""></igeo<>			
Level	1	2	3	4	5	6			
Pollution degree	Slight to non-pollution	Moderate pollution	Moderate to severe pollution	Severe pollution	Severe to utmost pollution	Utmost pollution			

TABLE 3: HEAVY METAL POLLUTION DEGREE CALCULATED VALUE OF SURFACE SOIL

Heavy metals	P _i (amplitude)	P _i (mean)	P _c	Level	Pollution degree
Cu	0.11-0.94	0.5	0.89	2	Warning
Cr	0.04-0.51	0.32	0.68	1	Normal
Pb	0.98-4.29	2.36	2.95	4	Moderate pollution
Zn	0.37-1.96	0.81	1.68	3	Slight pollution
Hg	0.03-0.38	0.19	0.41	1	Normal
Cd	0.92-10.88	6.17	10.62	5	Heavy pollution
As	0.06-0.89	0.46	0.93	2	Warning
Ni	0.03-0.58	0.34	0.75	2	Warning



Fig.1 Cumulative index weighted curve on heavy metal of surface soil

of these 4 kinds of heavy metals should be treated in time to prevent it from further expansion.

The cumulative exponential weighted variation curve of 8 kinds of heavy metals in the study area calculated according to Formula 3 is shown in Fig.1. As can be seen from the figure, of the 50 sampling points selected, those with a weighted value of the cumulative index below 5, that is, the non-extremely polluted soil accounts for 26% of the total; those with a weighted value of the cumulative index below 4, that is, the non-severely polluted soil accounts for 18% of the total; those with a weighted value of the cumulative index below 3, that is, the slightly polluted soil accounts for only 12%. It shows that the soil pollution around the metal mining area is more serious, with the pollution in most areas seriously exceeding the standard.

$3.2\ Evaluation$ of heavy metal pollution in soil profile

Fig.2 shows the vertical distribution of heavy metal content in soil around the metal mining area. As can be seen from the figure, except for the element Hg, the variation trends of the other 7 heavy metals with the increase of soil profile depth are basically the same, which means that the maximal value appears at the surface (0 cm), the content of heavy metals at the depth of 0-20 cm decreases sharply, and the content of each heavy metal at the depth ranging 20 cm-120 cm changes in a small extent and the final content tends to be stable. Specifically, the vertical distribution of Cd, Ni and



(a) Heavy metal content of Cd and Hg



(b) Heavy metal content of As, Cu and Ni



Fig.2 Heavy metal content variation of soil profile

Hg in soil varied greatly, whose content are 5.3%, 8.4% and 10% respectively, at a depth of 120cm; the vertical distribution of Zn and Cr varies less, and their content at the depth of 120cm is 26.2% and 23.5% of the content at the surface, respectively. According to the above analysis, we can see that heavy metals are mostly concentrated within a range of 10cm of the surface soil. With the increase of depth, the content of heavy metals drops sharply, when the depth exceeds 1m, the soil is clear of heavy metal pollution.

3.3 Evaluation of heavy metal pollution in different directions of the mining area

Fig.3 shows the content distribution curve of 8 heavy metals in the surface soil in 4 directions around the metal mining area. As can be seen from the figure, as a whole, the contents of heavy metals in the west and south of the metal mine are higher than those in the east and the north. Among them, the highest content of heavy metals in the west is 1.2



Fig.3 Heavy metal content variation with different direction in surface soil

times that of the east and 1.5 times that of the north. This may be because the prevailing downward wind in the west and south of the metal mine makes the heavy metal elements gradually to migrate to the western and southwestern regions. Due to the high contents of Ni, Pb, Zn and Cr in the soil, the enrichment characteristics in the western region and the migration characteristics of heavy metal elements from the east and the north to the west are more obvious.

3.4 MORPHOLOGICAL CHARACTERISTICS OF HEAVY METALS IN SURFACE SOIL

From the above analysis, it can be seen that the content of heavy metals in the surface soil around the metal mining area is the highest. Therefore, the existing forms and characteristics of heavy metals in the surface soil of the area are further analyzed. Five elements, including Cu, Ni, Pb, Zn and Cr whose contents are higher in the soil, were selected for analysis. Their metal morphological characteristics are as shown in Fig.4.

As can be seen in the figure, Cu, Ni, Pb, Zn and Cr are mainly in the residual form, accounting for 62%, 70%, 55%, 57% and 80% respectively of the overall form, followed by the oxidation form out of the rest 3 forms with an average value of 19.6%, then followed by reducible form, with an average value of 9.2%, and the proportion of the exchangeable form is the lowest, accounting for 6.4%. Zn element and Pb element can easily combine with the sulfur atom in the soil into sulfide precipitation. However, their reducible form is also relatively high and the two elements can be easily reduced to exchangeable form under certain conditions, causing secondary pollution to the surface soil. The average sum values of the residual and exchangeable forms of the above 5 elements can reach to more than 70%, thus they are easy to adsorb onto plants or humus and other objects on the surface soil, causing serious damage to the surrounding environment. Therefore, it is necessary to remove heavy metals from the soil surrounding the metal mining area as soon as possible.



1-Cu; 2-Ni; 3-Pb; 4-Zn; 5-Cr Fig.4 Speciation distribution of heavy metal in surface soil

4. Conclusions

Aiming at the problem of heavy metal pollution in soil surrounding the metal mining area, the heavy metal pollution is evaluated and studied from 4 aspects, including the surface soil around the metal mining area, the soil profile, and the different directions of the mining area and the morphological characteristics of heavy metals in the surface soil. The research conclusions are as follows.

- (1) The P_i and P_c values of Cd and Pb contained in soil are the highest in all heavy metals, which are rated as severe and moderate pollution respectively. The P_c values of Cr and Hg are less than 0.7, indicating that the surface soil in the study area is not polluted by them. The soil in the study area is slightly polluted by Cu, Zn, As and Ni. The calculation results of the cumulative exponential weighted values in the soil show that the soil pollution around the metal mining area is more serious, with the pollution in most areas seriously exceeding the standard.
- (2) The research results of vertical heavy metal distribution in soil show that heavy metals are mostly concentrated within a range of 10cm of the surface soil. With the increase of depth, the content of heavy metals drops sharply, when the depth exceeds 1m, the soil is basically clear of heavy metal pollution. As can be seen from the figure, as a whole, the contents of heavy metals in the west and south of the metal mine are higher than those in the east and the north. The content of heavy metals in the west is 1.2 times that of the east and 1.5 times that of the north. The prevailing downward wind in the west and south of the metal mine makes the heavy metal elements gradually to migrate to the western and southwestern regions.
- (3) Analysis of the morphological characteristics of heavy metals in surface soil shows that Cu, Ni, Pb, Zn and Cr are mainly in the residual form, accounting for 65.4% of the overall form, followed by the oxidation form with an average value of 19.6%, then followed by reducible form, with an average value of 9.2%, and the proportion of exchangeable form is the lowest, accounting for 6.4%. The average sum values of the residual and exchangeable forms of these 5 elements can reach to more than 70%, thus they are easy to adsorb onto plants or humus and other objects on the surface soil, causing serious damage to the surrounding environment.

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