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Contamination characteristics of heavy metals and enrichment capacity of native plants in soils around typical coal mining areas in Gansu, China

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Exploitation of mineral resources is a vital backbone of a country's socio-economic development. However, the coal exploration would cause ecological and environmental problems such as pollutions of water, soils and atmosphere. Especially, the pollution of heavy metals of soil has become increasingly severity. Plant enrichment and tolerance to heavy metals are crucial for the phytoremediation of coal gangue mountain. In phytoremediation, phytostabilization which can reduce the metal contamination of soil by uptake and burn-off of heavy metals with highly accumulating plants, is one of the most effective techniques of eco-remediation treatment. In present work, heavy metals contamination of soil and plants in the Yaojie mining which located in arid and semi-arid area of northwest China were investigated through field investigation. To identify the suitable plants for the remediation and ecological reclamation of heavy metal contaminated soil in typical mining area, the contamination characteristics of heavy metals in the above-ground parts of 27 native plants and their surrounding non-rhizosphere soils were analyzed. After eliminated by wet digestion and high-pressure closed digestion, the mass fractions of Zinc (Zn), cadmium (Cd), chromium (Cr) and copper (Cu) were determined with inductively coupled plasma emission spectrometer, and the contents of Hydrargyrum (Hg) and Arsenic (As) were analyzed with atomic fluorescence spectrophotometer. The Nemerow pollution index showed that in the surrounding soil, the pollution index of heavy metal was 6.32, which reached the extreme severe pollution level. Among the 6 heavy metals, the most severe contamination being Hg (Pi = 8.50) and had particularly strong Coefficient of variation (CV = 105.8%), which is more likely to be caused by anthropogenic activities. In the aboveground parts of 27 plants, except for Zn, other metals exceeded the standard level, and the exceedance rates in descending order were As, Hg, Cr, Cd, and Cu. The most severe exceedance of As was found in C. virgata, which was as high as 19.20, and the average exceedance rate of As in all plants was 2.79. Bioconcentration Factor (BCF) was utilized as an indicator of the enrichments of various metals in 27 plants. The maximum value of BCF for As and Hg in C. virgata were 1.52 and 2.50, Cr and Cu in X. sibiricum were 0.72 and 2.32, Cd and Zn in S. glauca were 3.33 and 1.82. As revealed, except Cr, all the BCF of other metals are greater than 1, indicating that the three plants exhibited a strong accumulation capacity of heavy metal and are potential candidate pioneer species for the removal of heavy metals from the contaminated soil in the Yaojie mining area. This study provides a basis for plant selection for ecological restoration of contaminated soils in arid and semi-arid regions.

Keywords Heavy metals pollution, Phytoremediation, Native plants, Enrichment capacity, Ecological restoration

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The development of mineral resources has greatly promoted economic development, and it has also brought environmental pollution problems¹. Especially the release and migration of various heavy metal elements accumulated in the mining area and surrounding soil caused regional heavy metal pollution and ecosystem damage, and through contact, respiration, and food chain amplification, it seriously threatened the soil health and biodiversity^{2,3}. Due to their high toxicity, persistent nature, and bioaccumulative nature, heavy metals have been listed as priority pollutants of ecological environment⁴. Heavy metal pollution in the gangue-soil–plant system in coal mining areas has become a public concern. Therefore, it is very important to carry out ecological restoration and management of polluted environment in coal mining areas.

With the characteristics of low degradation, strong concealment, and high toxicity in natural environment, heavy metals are considered as the main pollutants in soil, which can be transferred to food chain through crops. So far, physical, chemical, biological, and even combined remediation technologies have been applied to remove the heavy metals from contaminated soil^{5,6}. Among the above methods, the phytoremediation has attracted much attention due to its sustainability, environmental friendly, cost-effective and easy of large-scale rollout^{7–10}. According to the processes and mechanisms of phytoremediation, the remediation technologies for heavy metal contaminated soils include phytostabilisation, phytoextraction (Hyperaccumulator) and pyhtovolation etc. 11. Although most populations of plants are susceptible to metal elements that cause tissue damage or even mortality at high enrichments, there are some populations that are tolerance to heavy metal stress¹². The plants which can accumulate the toxic heavy metals in their parts especially roots and shoots are classified as accumulators and hyperaccumulators^{13,14}. The hyperaccumulation value for a certain plant is based on the threshold 'maxima' at which the plant can safely ingest/absorb an element from soils without tissue damage^{15,16}. The determination of the thresholds for hyperaccumulator is referred to Purwadi et al. 16, e.g., As (8 mg·kg⁻¹), Zn (181 mg·kg⁻¹). Selection of suitable hyperaccumulator for ecological remediation is an effective strategy to address the ecological damage in mining areas. Nowadays, the evaluation of soil heavy metal contamination is generally based on the Single Factor Contamination index, the Nemerow pollution index and the geo-accumulation index, etc. 17. While the heavy metal accumulation capacity of plants is usually indicated by bioconcentration factor (BCF) and translocation factor (TF)¹⁸. Zhang et al. analyzed the dominant plants in the Lanping lead–zinc mining area in the Yunnan Plateau and found that C. yanhusuo, P. hieracioides and C. bretschneideri have a strong ability to accumulate Cd1. He et al. (2013) studied the lead-zinc tailings reservoir in Xiashuiwan, Hunan, and found that the Pb content of the above-ground part of Loquat is seriously exceeding the standard, with an bioconcentration factor of 14.4, which can be used as a target plant for the remediation of contaminated soil in the reservoir area 19. Chen et al. pointed out that Xanthium strumarium, Artemisia scoparia Waldst, Artemisia mongolica and Setaria viridis exhibit a strong ability to accumulate multiple metals (Cd-Cr-Pb-Cu) from contaminated soil in the coal mine wasteland²⁰. Wang et al. analyzed the contents of heavy metals in different parts of 53 plant species in Bayan Obo coal mining area of Inner Mongolia and indicated the bioconcentration factor of S. collina to Cu and Hg, A. argyi and S. japonica to Cu were all greater than 1, which belong to the enrichment plants²¹. The work of Li et al. showed that the Pteris multifida and Trachelospermum jasminoides are hyperaccumulators for Cd, Cr, Cu, Mn, Pb, and Zn²². Yu et al. evaluated the contents of heavy metals in soil-crops of a cultivated field around a mining area in Chongqing with Nemerow index and found that heavy metals concentrated to a moderate degree in the tillage soil (0-20 cm), and the Cd and Hg contents in rice, maize and sweet potato exceeded the Chinese food standards²³. A comprehensive analysis shows that the selection of local dominant hyperaccumulating plants is of great value and significance for the treatment of heavy metal environmental pollution and ecological restoration and reconstruction.

The Yaojie mining area in Gansu Province is one of the "Top 100 National Coal Industries in China". In recent years, most of the researches on mining areas are focused on the coal quality characteristics of the mining area and the greenhouse gases produced²⁴. While studies about the evaluation of soil pollution and the investigation of native plants are rare, and the tolerance and accumulation capacity of plants in mining areas with serious soil pollution to heavy metals are still not well understood. In order to screen out the dominant plants with strong capacity of absorbing and accumulating heavy metals with adapted to local climate and soil conditions, 27 plants and the surrounding non-rhizosphere soils in Yaojie mining were adopted as the research objects in present study. The aim is to provide a theoretical basis for guiding soil and ecological restoration in research areas and similar mining areas.

Materials and methods Overview of the study area

Yaojie coal mining, consisting of the Yaojie Sankuang mine and Haishiwan mine (Fig. 1), is one of the key coal bases in Gansu Province. It is located in Honggu District of Lanzhou City at the border of Gansu and Qinghai, northwest of Loess Plateau, and the upper reaches of the Yellow River, between 32°31′ ~ 42°57′N, 92°13′ ~ 108°46′E. East–West Environmental Protection by Mt. Haragu and Mt. Majiling. The landform type is gray-white, gray-black claystone, carbonaceous industrial rock, fine sandstone, fine conglomerate, thin coal seam and oil shale deposited in river-marsh facies. The temperature is in the range of –23 to 35°C, the annual rainfall is 200–300 mm, and the annual evaporation is 1300–2100 mm. The Datong River through the Yaojie coal mining area from north to south 25,26. The main soil types in the region are gray calcium soil, yellow brocade soil, irrigated soil and tidal soil. The main plants include: S. collina, K. scoparia, Pottasche, C. virgata, A. lavandulaefolia, X. sibiricum, D. stramonium, A. splendens, H. taraxaci, C. hederacea, S. glauca, C. epigeios, C. album, A. capillaris, C. chinense, Lycium, S. viridis, R. acetosa, C. bipinnata, E. dahuricus, A. tricolor, U. pumila, S. japonica, P. harmala, K. integrifolia, A. annua and E., sinica.

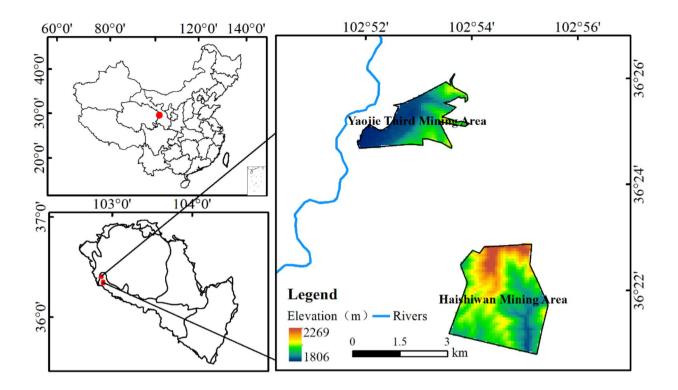


Fig. 1. Overview map of the study area (ArcGIS Desktop 10.2, https://www.esri.com/en-us/home).

Sample collection and processing

Soil samples were collected according to the technical specifications for soil environmental monitoring by using the tessellation method of sampling. In November 2021, surface layer (0-20 cm) soil samples were collected from the study area of Yaojie Coal Mine, and GPS was used to locate the sampling points. The collection of soil samples were conducted by the double diagonal five-point sampling method. The raw soils were mixed into a positive sample with weight of approximately 1000 g. After air-dried, ground and sieved, 78 representative soil samples (47 samples from the Sankuang mine and 31 samples from the Haishiwan mine) were selected for analyzation of heavy metal content. Plant samples were collected from the above-ground part, with a total of 27 plant samples (21 samples from the Sankuang mine and 6 samples from the Haishiwan mine). The plant samples were collected from the above-parts of the dry plants.

The collected soil samples were dried with reference to the Specification for Geochemical Evaluation of Land Quality DZ/T0295—2016. Soil samples were processed by placing the retrieved soil samples indoors to dry naturally, and then the residual roots, rocks and other debris in the samples were removed from the samples. After air-drying naturally, the soils were crushed with a thin wooden stick, and then ground in a mortar. After passing through a 100-mesh nylon screen, 200 g of the soil sample was sealed and stored in a ziplock bag. The indoor treatment of the plant samples was done by first rinsing off the dust and soil from the plant surface with tap water. Then the plant was rinsed with distilled water for 3 times, and finally rinse with deionized water 3 times. The plant sample was put in a paper envelope, and placed in an oven at 105 °C for 30 min. The plant samples were dried at 60 °C in a drying case to constant weight. After the sample was pulverized with sample grinding machines, it was passed through a 100-mesh nylon sieve and put into a ziplock bag and sealed for storage²⁷.

Sample analysis and testing methods

The samples were washed, air-dried, milled into powder, and then sieved through a 100-mesh sieve. The soil samples were decomposed using $\mathrm{HCl-HNO_3-HClO_4-HF}$, and the plants samples were digested using $\mathrm{HNO_3}$ and $\mathrm{H_2O_2}$. The concentrations of Cd, Cr, Cu, and Zn were measured by inductively coupled plasma mass spectrometry (ICP-MS, Thermo X-SERIES2) and those of Hg and As were measured by Atomic fluorescence spectrophotometer (AFS, Haiguang AFS-3100). Soil basic properties, such as soil pH, soil nutrients, soil organic matter (SOM), and cation exchange capacity (CEC), have been studied because they are key factors that influence the transport, transformation and enrichment of heavy metals in soil²⁸. The soil pH was detected using the ion-selective electrode method with a soil to water ratio of 1:2.5. Soil organic matter (SOM) was measured using the oxidized method with potassium dichromate; The cation exchange capacity (CEC) was determined using the Ammonium acetate titration method. Soil conductivity is determined by the electrode method. Soil total nitrogen, total phosphorus, and total potassium were determined by kjeldahl nitrogen determination,

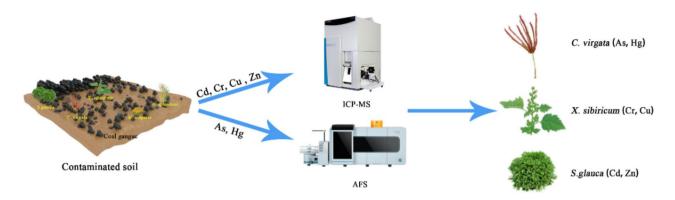


Fig. 2. Research flowchart.

P_{i}	P _{com}	Pollution level
≤0.7	≤0.7	Clean (I)
0.7 ≤ 1.0	0.7 ≤ 1.0	Relatively clean (II)
1.0 ≤ 2.0	1.0 ≤ 2.0	Mild pollution (III)
2.0 ≤ 3.0	2.0 ≤ 3.0	Moderate pollution (IV)
> 3.0	> 3.0	Severe Pollution (V)

Table 1. Criteria for the classification of soil potentially toxic elements pollution.

decoction-molybdenum antimony antimony colorimetric method and flame photometric method, respectively. The accuracy and precision of the soil sample analyses were in accordance with the required specifications²⁷. The research flow chart for this study is shown in Fig. 2.

The evaluation of soil heavy metal pollution usually adopts the single factor pollution index method and the Nemeiro comprehensive pollution index method²⁹. The bioconcentration factor (BCF) was used to analyze the heavy metal accumulation capacity of plants³⁰.

According to single factor index method, the natural background value of soil in Gansu Province was selected as the standard to evaluate the environmental quality of soils contaminated with heavy metals in the study area, which can directly reflect the pollution of the heavy metals. The formula is:

$$P_i = C_i/S_i$$

where: P_i is the single-factor pollution index of heavy metal i; C_i is the measured value of the concentration of heavy metal i, $mg\cdot kg^{-1}$; S_i is the standard value of heavy metal i.

Nemeiro Comprehensive Pollution Index Method, is the most widely used method for evaluating soil heavy metal pollution which can fully reflect the comprehensive impact of heavy metals on the soil, effectively avoiding the weakening of the weight of heavy metals caused by the average^{17,23}. The formula is:

$$P_{com} = \sqrt{\frac{(P_{\text{max}}^2 + P_{\text{ave}}^2)}{2}}$$

where: P_{com} is the Nemeiro comprehensive pollution index; P_{max} is the maximum single factor pollution index; P_{ave} is the arithmetic mean of the single factor pollution index.

According to the single factor pollution index and Nemeiro comprehensive pollution index, the heavy metal pollution in soils is divided into 5 levels²², as shown in Table 1.

The bioconcentration coefficient (BCF) is the ratio of the mass fraction of heavy metals in the plant to the corresponding mass fraction of heavy metals in the soil. It reflects the difficulty of the plant to absorb and accumulate heavy metals in the soil, and is an evaluation index for the ability of plants to accumulate heavy metals. When BCF>1, the heavy metal content in the plant is greater than the heavy metal content in the soil environment where the plant grows, and it can be used for soil heavy metal pollution remediation. Excess multiples of heavy metals in plants (TON) is calculated using the normal content of plants as the reference value ^{18,31,32} to measure the relative degree of plant pollution. The formula is:

$$BCF = \omega/\omega_{soil}$$

$$TON = \omega/\omega_{\rm plant}$$

No	Native Species	Family	Genus	Abundance
1	S. collina	Chenopodiaceae	Salsola	Moderate
2	K. scoparia	Chenopodiaceae	Kochia	Rare
3	Pottasche	Chenopodiaceae	Suaeda	Moderate
4	C. virgata	Poaceae	Chloris	Abundant
5	A. lavandulaefolia	Asteraceae	Artemisia	Abundant
6	X. sibiricum	Asteraceae	Xanthium	Abundant
7	D. stramonium	Solanaceae	Datura	Rare
8	A. splendens	Poaceae	Achnatherum	Abundant
9	H. taraxaci	Asteraceae	Sonchus	Abundant
10	C. hederacea	Convolvulaceae	Calystegia	Rare
11	S. glauca	Chenopodiaceae	Suaeda	Abundant
12	C. epigeios	Poaceae	Bromus	Few
13	C. album	Chenopodiaceae	Chenopodium	Abundant
14	A. capillaris	Asteraceae	Artemisia	Abundant
15	C. chinense	Asclepiadaceae	Cynanchum	Few
16	Lycium	Solanaceae	Lycium	Rare
17	S. viridis	Poaceae	Setaria	Moderate
18	R. acetosa	Polygonaceae	Rumex	Rare
19	C. bipinnata	Asteraceae	Callistephus	Fewer
20	E. dahuricus	Poaceae	Elymus	Rare
21	A. tricolor	Amaranthaceae	Amaranthus	Rare
22	U. pumila	Ulmaceae	Ulmus	Rare
23	S. japonica	Poaceae	Setaria	Few
24	P. harmala	Zygophyllaceae	Tribulus	Few
25	K. integrifolia	Asteraceae	Kalimeris	Moderate
26	A. annua	Asteraceae	Artemisia	Abundant
27	E. sinica	Ephedraceae	Ephedra	Moderate

 Table 2. Introduction to the dominant plant species in the Yaojie Coal Mining Area.

Measurement indicators	pН	Organic matter	Conductivity	cation exchange capacity	Total nitrogen	Total phosphorus	Total Potassium
Average content	8.69	25.77 g/kg	0.39 ms/cm	4.44 cmol(+)/kg	0.74 g/kg	0.51 g/kg	16.65 g/kg

Table 3. Basic physical and chemical properties of soils in the Yaojie Coal Mining Area.

In the formula, BCF and TON are the bioconcentration factor and the heavy metal exceeding multiple in the plant; ω_{voil} , ω_{soil} , ω_{plant} are plant, soil, and normal heavy metal mass fractions in the plant, mg·kg⁻¹, respectively.

Result and discussion Composition of plant families and genera

A total of 27 native plant species, belonging to 25 genera and 11 families, were investigated in the selected samples in the study area. Among them, 7 species of *Asteraceae* (31.8%), 6 species of *Poaceae* (22.2%), 5 species of *Chenopodiaceae* (18.5%), 2 species of *Solanaceae* (7.4%), and 1 species each of *Zygophyllaceae*, *Polygonaceae*, *Asclepiadaceae*, *Amaranthaceae*, *Convolvulaceae*, *Ulmaceae* and *Ephedraceae*, each of which accounted for 3.7%. The dominant plant species in the Yaojie Coal Mine Area are described in Table 2.

From the information provided in Table 2, nine species of dominant plants with higher frequency and greater multiplicity of occurrence in the sample area were selected, including *S. glauca, C. album, A. splendens, A. lavandulaefolia, C. virgata, A. capillaris, A. annua, H. taraxaci, and X. sibiricum,* among which five species of Asteraceae accounted for 55.6%, and due to the fact that Asteraceae has the characteristics of tolerance to cold, drought, salinity, and infertility, the plants in the Yaojie Coal Mining Area of western China occupies a clear advantage and has a stronger ability to adapt to the environment of the region.

Characterization of heavy metal pollution in soil

The basic physical and chemical properties of the soil in the Yaojie coal mine area are shown in Table 3. The study area's soil exhibits an abundance of heavy metals, as evidenced by Table 4, with the content of the 6 heavy metals displaying a substantial range of fluctuations. The mass fraction ranges of As, Cd, Cr, Cu, Hg and Zn in the soil of Yaojie mining area were 23.01–34.13, 0.14–0.30, 67.38–153.69, 18.69–49.19, 0.01–0.47 and 44.28–128.80 mg·kg⁻¹, with average values of 28.08, 0.23, 106.67, 31.02, 0.17, and 82.03 mg·kg⁻¹, respectively.

Element	As	Cd	Cr	Cu	Hg	Zn
Max	34.13	0.30	153.69	49.19	0.47	128.80
Min	23.01	0.14	67.38	18.69	0.01	44.28
Mean	28.08	0.23	106.67	31.02	0.17	82.30
Coefficient of variation, CV(%)	12.8	29.08	31.94	42.7	105.8	43.9
Gansu soil background value stantard	12.60	0.12	70.20	24.10	0.02	68.50
China Soil Environmental Quality Standard (pH > 7.5)	25	0.6	250	100	3.4	300
TOB	1.23	0.92	0.52	0.29	7.50	0.20
P_i	2.23	1.92	1.52	1.29	8.50	1.21
P _{com}	6.32					

Table 4. Mass fraction of heavy metals and pollution index of soils in the Yaojie Coal Mining Area(mg/kg). TOB is the value of the pollution index calculated by the soil background value of Gansu province (National Environmental Protection Agency, 1990), Average over-standard multiple = (average value-evaluation standard value)/evaluation standard value.

The average content of heavy metals in soil in this area is lower than the screening value of soil pollution risk in agricultural land. The average contents of As, Cd, Cr, Cu, Hg and Zn are higher than the soil environmental background values, which are 1.23, 0.92, 0.52, 0.29, 7.50 and 0.20 times of the background value, respectively. This indicates that regional soils accumulate different levels of heavy metals due to the combined influence of unique geological background and human production activities³³.

The magnitude of the coefficient of variation reflects the extent of external interference of heavy metals in soil³³. In this study area, the coefficients of variation for the six elements showed differences, with Hg showing the most significant coefficient of variation (105.8, CV > 100%), while the others exhibited moderate variations (10% < CV < 100%). This indicates that the spatial distribution of elements (especially Hg) in this region is highly discrete which may likely be due to the interference of human factors.

Based on the single-factor pollution index, the classification of Cr, Cu and Zn are between relatively clean and mild pollution, indicating the possibility of pollution. As and Cd exhibited moderate pollution, while Hg showed the most serious pollutant. The degree of Hg pollution varies greatly in this study area, so the remediation of Hg pollution should be prioritized in the future (Fig. 3), which agrees well with the conclusions of Wu et al. 34 and Xue et al. 35 . The results showed that the pollution level of 6 heavy metals in soil was Hg > As > Cd > Cr > Cu > Zn. The Nemerow comprehensive pollution index in the study area was 6.32, which reached the level of heavy pollution.

Heavy metal content in native plants

The contents of As, Cd, Cr, Cu, Hg and Zn in the 27 native plants were measured (Table 5 and Fig. 4). The plants with No. 1-21 were from San-kuang Mine (SK Mine) and which with No. 22-27 were from Haishiwan Mine (HSW Mine). The mean values of mass fractions of heavy metals were 2.78, 0.13, 9.78, 14.54, 0.02 and 49.54 mg·kg-1, in the order of from high to low is Zn > Cu > Cr > As > Cd > Hg. The mass fractions of heavy metals in all plants were in the range of 5.67-125.00 mg·kg⁻¹ for Zn, 3.05-56.00 mg·kg⁻¹ for Cu, 0.61-50.40 mg·kg⁻¹ for Cr, 0.22-19.20 mg·kg⁻¹ for As, 0.03-0.40 mg·kg⁻¹ for Cd, and 0.01-0.05 mg·kg⁻¹ for Hg, respectively. The contents of As and Hg were highest in *C. virgata* among all plants, with mean concentrations of 19.2 and 0.05 mg·kg⁻¹, Cr and Cu in *X. sibiricum*, with mean concentrations of 50.40 and 56.00 mg-kg⁻¹, and Cd and Zn in *S. glauca*, with mean concentrations of 0.40 and 125.00 mg-kg⁻¹.

Compared with the normal content of heavy metals in plants, the content of heavy metals in the 27 dominant plants was different. Except for the content of Zn, the content of other heavy metals, As, Cd, Cr, Cu and Hg, all exceeded the normal range to varying degrees (Table 6).

In the above-ground parts of all 27 plants in the Yaojie coal mine, the maximum exceedance value of element As was the highest (19.20), followed by Cr (6.00), Hg (4.00), Cd (2.00) and Cu (1.87), and finally Zn (0.83). The exceedance value of Zn in all plants was below 1, while the value of other elements varied greatly depending on the plant. The average exceedance of As in the above-ground parts of all plants was 2.79 times, with the highest exceedance of As in C. virgata at 19.20 times, followed by A. lavandulaefolia, X. sibiricum and H. taraxaci at 10.7, 6.57 and 5.46 times, respectively. Based on the order of Cr exceedance, the highest to the lowest were X. sibiricum (6), C. virgata (5.38), K. integrifolia (2.36), and A. tricolor (2.17). The exceedance of Hg in C. virgata was 4, which was twice as high as that in X. sibiricum, A. capillaris and K. integrifolia. While in 12 plants (K. scoparia, Pottasche, C. hederacea, S. glauca, C. chinense, Lycium, R. acetosa, E. dahuricus, U. pumila, S. japonica, A. annua, E. sinica), Hg was not detected. As for Cd, the most significant exceedance was found in S. glauca with two times of exceedance, followed by Pottasche and A. capillaris with 1.25 and 1.10 times of exceedance, respectively; The most significant exceedance of Cu in X. sibiricum was 1.87 times, followed by S. viridis with 0.98 times; In all plants, the exceedance of Zn was not significant, with the largest exceedance of 0.83 times for S. glauca, followed by 0.64, 0.58, 0.57 and 0.56 for C. virgata, H. taraxaci, S. viridis and C. hederacea, respectively. Overall, the contents of heavy metals in the plants were basically consistent with those in the soil.

Among the 27 plants in this study, 5 plants, *Lycium, R. acetosa*, *E. dahuricus*, *U. pumila and S. japonica*, displayed exceedances of heavy metals As, Cd, Cr, Cu, Hg and Zn below 1, indicating that it was an excluder of heavy metals. Moreover, no Hg was detected in any of these plants, indicating that they exhibited a weak adsorption capacity for the above-mentioned heavy metals. Therefore, the 5 above-mentioned plants are not

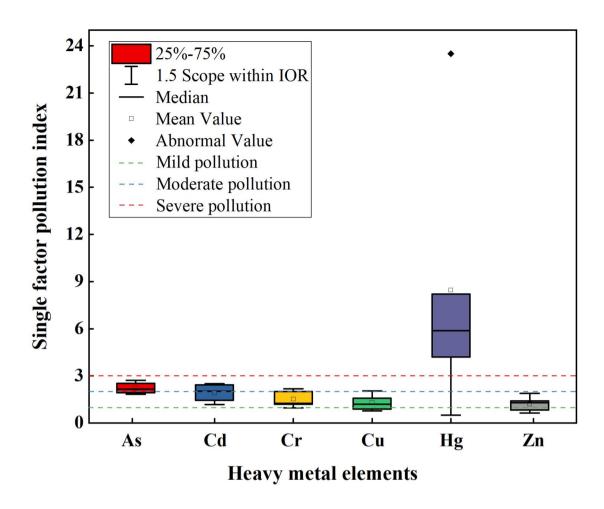


Fig. 3. Single factor pollution index of heavy metals in soil around Yaojie Coal Mining Area.

suitable as target plants for ecological soil environment restoration of the mines in the northwest arid and semiarid regions represented by the Yaojie coal mine. In contrast, *C. virgata* exhibited the most severe exceedances of As and Hg, with 19.20 and 4 times, respectively, which accounted for the highest exceedance of As among all plants; *X. sibiricum* showed the highest exceedance of As, Cr and Cu, up to 6.57, 6 and 1.87 times, respectively, being the only plant with Cu exceedance among all plants; *S. glauca* exhibited the most significant exceedance of Cd and Zn with 2 and 0.83 times, respectively. Previous studies have shown that *A. cepacia* can improve the remediation efficiency of agricultural fields polluted with Cd and As³⁶, and can also effectively rehabilitate Cd-PAHs complex contaminated soils³⁷. Another study showed that *A. cepacia* displayed a good enrichment capacity and tolerance to Cd³⁸. The work of Han et al. showed that *S. glauca*, *C. dactylon*, *P. australis* and *S. Purslane* also have a good enrichment capacity for various heavy metals³⁹. Studies conducted by Zhang⁴⁰ and Dong et al.⁴¹ showed that *S. glauca* high capacity for Cd accumulation and soil remediation. The work of Wan et al. showed that *S. glauca* are also highly tolerant to Cu and Ni. The present study is in accordance with these findings⁴².

According to Zhang, *S. glauca* exhibited a remarkable accumulation ability and tolerance to Cd⁴⁰. Moreover, *S. glauca* showed a better tolerance capacity for Cd, Pb and Mn compared to *Arabidopsis*⁴³. The Zn content in *S. glauca* plants was significantly higher than that of *B. campestris* plants⁴⁴. All of the above studies concluded that *S. glauca* has a strong enrichment capacity for Cd. *C. virgata*, *X. sibiricum*, and *S. glauca* are promising candidates as supporting plants in the remediation of soils contaminated with multiple heavy metals. Although these plants show potential, they still exhibit a certain margin of improvement compared to the updated threshold Hyperaccumulator found by previous studies in coal mining areas^{20,32}. This suggests that further research and selection may discover more effective plant species in studied aera.

The content of heavy metals in plants in SK mine was higher than that in HSW mine (Fig. 5). Moreover, the content of Pb in both the SK mine and HSW mine was low, indicating that the Pb pollution was slight, while the content of Zn was significantly higher for both mines, which implies that the level of Zn pollution was unduly high; The As content of the three mines was significantly higher than that of HSW mine, indicating that the As

		As	Cd	Cr	Cu	Hg	Zn
No	Native plant species	(mg kg ⁻¹)	(mg kg-1)	(mg kg-1)			
1	S. collina	1.04	0.13	3.86	11.30	0.02	32.20
2	K. scoparia	0.88	0.16	1.15	5.74	0.01	15.80
3	Pottasche	1.89	0.25	7.99	15.20	0.01	43.70
4	C. virgata	19.20	0.21	45.20	25.20	0.05	95.50
5	A. lavandulaefolia	10.70	0.19	8.19	10.40	0.02	39.60
6	X. sibiricum	6.57	0.09	50.40	56.00	0.03	64.70
7	D. stramonium	1.38	0.08	4.77	15.90	0.02	53.70
8	A. splendens	0.69	0.03	1.44	3.45	0.02	17.80
9	H. taraxaci	5.46	0.17	15.20	23.50	0.02	86.40
10	C. hederacea	1.82	0.10	6.74	15.00	0.01	83.50
11	S. glauca	3.90	0.40	11.3	16.80	0.01	125.00
12	C. epigeios	2.20	0.06	5.60	5.67	0.02	46.30
13	C. album	1.74	0.16	10.80	16.40	0.02	66.60
14	A. capillaris	3.07	0.22	9.24	16.20	0.03	45.70
15	C. chinense	1.19	0.04	4.54	8.57	0.01	35.70
16	Lycium	0.23	0.09	0.99	24.20	0.01	45.40
17	S. viridis	1.73	0.13	6.63	29.30	0.02	84.90
18	R. acetosa	0.22	0.03	0.61	3.05	0.01	5.67
19	C. bipinnata	1.23	0.07	7.08	7.38	0.02	50.80
20	E. dahuricus	0.46	0.05	0.80	3.18	0.01	15.10
21	A. tricolor	1.99	0.09	18.20	8.16	0.02	38.30
22	U. pumila	0.61	0.07	2.82	12.20	0.01	57.20
23	S. japonica	0.80	0.11	5.03	6.63	0.01	26.60
24	P. harmala	0.73	0.12	3.68	8.72	0.02	17.70
25	K. integrifolia	1.93	0.15	19.80	19.10	0.03	57.50
26	A. annua	2.37	0.16	5.74	7.84	0.01	19.00
27	E. sinica	1.18	0.13	6.14	17.60	0.01	67.30
	Mean	2.78	0.13	9.78	14.54	0.02	49.54
	Stardand content	< 1.00	0.05~0.20	0.20~8.40	5~30.00	< 0.10	27~150.00

Table 5. Mass fractions of heavy metals in 27 native plants in the Yaojie Coal Mining Area.

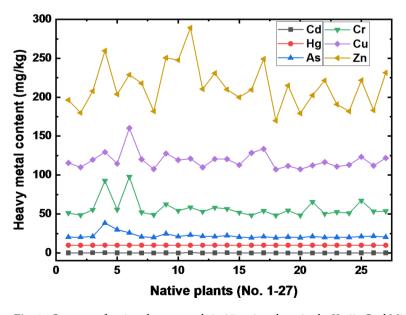


Fig. 4. Contents of various heavy metals in 27 native plants in the Yaojie Coal Mining Area.

	As	Cd	Cr	Cu	Hg	Zn
Native plant species	TON	TON	TON	TON	TON	TON
S. collina	1.04	0.65	0.46	0.38	1.00	0.21
K. scoparia	0.88	0.80	0.14	0.19	NE	0.11
Pottasche	1.89	1.25	0.95	0.51	NE	0.29
C. virgata	19.20	1.05	5.38	0.84	4.00	0.64
A. lavandulaefolia	10.70	0.95	0.98	0.35	1.00	0.26
X. sibiricum	6.57	0.45	6.00	1.87	2.00	0.43
D. stramonium	1.38	0.40	0.57	0.53	1.00	0.36
A. splendens	0.69	0.15	0.17	0.12	1.00	0.12
H. Taraxaci	5.46	0.85	1.81	0.78	1.00	0.58
C. hederacea	1.82	0.50	0.80	0.50	NE	0.56
S. glauca	3.90	2.00	1.35	0.56	NE	0.83
C. epigeios	2.20	0.30	0.67	0.19	1.00	0.31
C. album	1.74	0.80	1.29	0.55	1.00	0.44
A. capillaris	3.07	1.10	1.10	0.54	2.00	0.30
C. chinense	1.19	0.20	0.54	0.29	NE	0.24
Lycium	0.23	0.45	0.12	0.81	NE	0.30
S. viridis	1.73	0.65	0.79	0.98	1.00	0.57
R. acetosa	0.22	0.15	0.07	0.10	NE	0.04
C. bipinnata	1.23	0.35	0.84	0.25	1.00	0.34
E. dahuricus	0.46	0.25	0.10	0.11	NE	0.10
A. tricolor	1.99	0.45	2.17	0.27	1.00	0.26
U. pumila	0.61	0.35	0.34	0.41	NE	0.38
S. japonica	0.80	0.55	0.60	0.22	NE	0.18
P. harmala	0.73	0.60	0.44	0.29	1.00	0.12
K. integrifolia	1.93	0.75	2.36	0.64	2.00	0.38
A. annua	2.37	0.80	0.68	0.26	NE	0.13
E. sinica	1.18	0.65	0.73	0.59	NE	0.45

Table 6. Exceeding the standard of heavy metals in 27 plants in the Yaojie Coal Mining Area. NE means not exceeding the standard.

pollution in the three mines was more serious. This suggests that the regional soils have accumulated different levels of heavy metals due to anthropogenic impacts 1,20.

The enrichment characteristics of heavy metals in plants

The overall performance of the 27 plants for the BCF of heavy metals was Cd> Hg> Zn> Cu> As> Cr (Fig. 6), the SK Mine was stronger than the HSW Mine. The BCF value of *C. virgata* to As reached 1.52, and the rest of the plants were less than 1. All plants had obvious differences in the absorption capacity of Cd, and the maximum BCF value of *S. glauca* to Cd was 3.33, followed by 3, indicating that *S. glauca* has the strongest enrichment capacity for Cd, while other plants had weaker ability; The BCF of all plants did not exceed 1 for Cr, and the maximum BCF was only 0.72 for *X. sibiricum*, indicating that they had sensitive to Cr. The BCF of *X. sibiricum* reached a maximum of 2.32 for Cu, followed by *S. viridis* with a BCF value of 1.22, and *C. virgata* and *Lycium* also had some absorption capacity for Cu with BCFs of 1.05 and 1, respectively; 27 plants had different enrichment capacities to Hg, and the strongest enrichment capacity for Hg was found in *C. virgata*, with a maximum BCF value of 2.5 times. The enrichment capacity of Zn of *C. virgata*, *H. taraxaci*, *C. hederacea*, *S. glauca* and *S. viridis* were more than 1, 1.39, 1.26, 1.22, 1.82, 1.24 times, respectively, and *S. glauca* had the best enrichment capacity of Zn among them. To sum up, *C. virgata* had the strongest enrichment capacity for As and Hg, *X. sibiricum* for Cr and Cu, and *S. glauca* for Cd and Zn. *C. virgata*, *X. sibiricum*, and *S. glauca* have good restoration potential for As and Hg, Cr and Cu, Cd and Zn, respectively, and can be used as supporting plants.

Pearson correlation analysis of heavy metal content in soil and native plants

Pearson correlation analysis ($p \le 0.05$) of heavy metal contents in the above-ground parts of 27 indigenous dominant plants with heavy metal contents in the soil of Yaojie coal mine. Figure 7 shows that soil Cd and Cr contents exhibited a statistically significant positive correlation (0.60 and 0.60, 0.55 and 0.55, 0.54 and 0.54) with Hg, As and Cr contents in the aboveground parts of the plants, respectively, and soil Hg content also showed a significant positive correlation (0.51) with Hg content in the plants, The elemental content of Cd, Cr in the soil is more closely related to elements except Cd in the plant; Zn content and pH in the soil showed a significant negative correlation (-0.41,-0.37) with As and Hg content of the aboveground parts of the plants, respectively, whereas its relationship with the other elements is statistically negligible. The activity and transport of soil certain heavy metals can be influenced by soil pH, hence resulting in the enrichment of heavy metals⁴⁵.

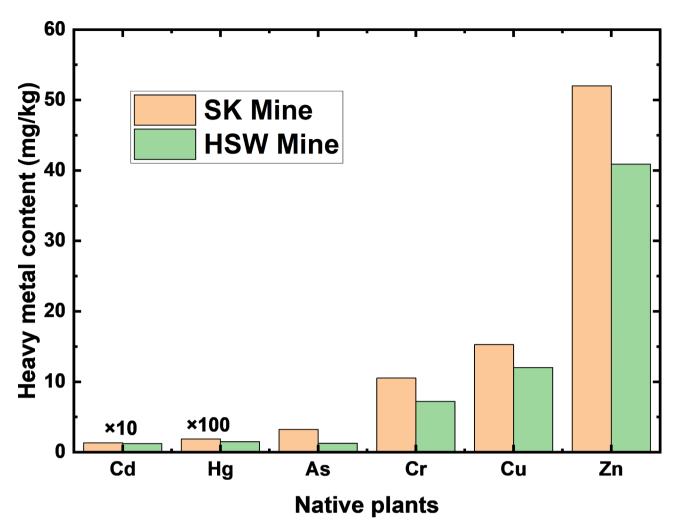


Fig. 5. Comparison of heavy metals contents in plants from SK Mine and HSW Mine.

The investigation revealed a statistically Significant positive correlation among the elements, indicating a potential common origin, which aligns with previous analysis. The observed robust association between the elements implies that these elements could potentially be influenced by both the soil-forming parent material and transportation activities in coal mining area. This finding aligns with the empirical findings obtained within the study region.

The coal mining area is a complex ecosystem composed of resources, environment, social economy, etc. The ecological environment is severely damaged, heavy metal content is high, and nutrient elements are lacking, which severely restricts the growth and development of plants. However, suitable native dominant plants and super-enriched plants can be screened to effectively improve the soil environment and restore the vegetation coverage⁴⁶. This study found that there is a strong correlation between soil heavy metal content and plant heavy metal, and the basic characteristics are also the same, which is consistent with the results of Zhang et al.⁴⁰. The absorption of heavy metal elements by the plants is not only affected by the heavy metal content of the soil, plant characteristics, soil quality, morphology, and toxicity of soil heavy metals, but also related to the terrain condition, synergistic effect produced by physicochemical properties and compound pollution of the synergy effect. Plants have gradually become tolerant to heavy metals in order to adapt to the complex environment, but each plant has different adaptability and resistance to various heavy metals²².

In this study, three plant species (*C. virgata, X. sibiricum* and *S. glauca*) were screened as possible candidates for the treatment of heavy metal pollution and restoration of ecological environment in the Yaojie coal mine area. Possibly due to the special rhizomatous effect of these three plants, the morphology of heavy metals and the physicochemical properties of the soil are altered, thus increasing the enrichment capacity of the plants⁴³. Unfortunately, low contamination levels of heavy metal contamination (Cd, Cu and Zn) in the soils of the study area may limit the applicability of the results. Although heavy metals in plants are closely related to the heavy metal content in soil, the plant's growth performance and ability to thrive under contaminated conditions, the physical and chemical properties of the soil, and economic costs should also be taken into account³⁶. In addition, the plants used for heavy metals decontamination often tend to return heavy metals elements to the soil through decay and defoliation, so the re-processing of plants that accumulate a large amount of heavy metals was also a thorny issue. Thus the plants must be harvested before they drop their leaves and promptly rendered harmless

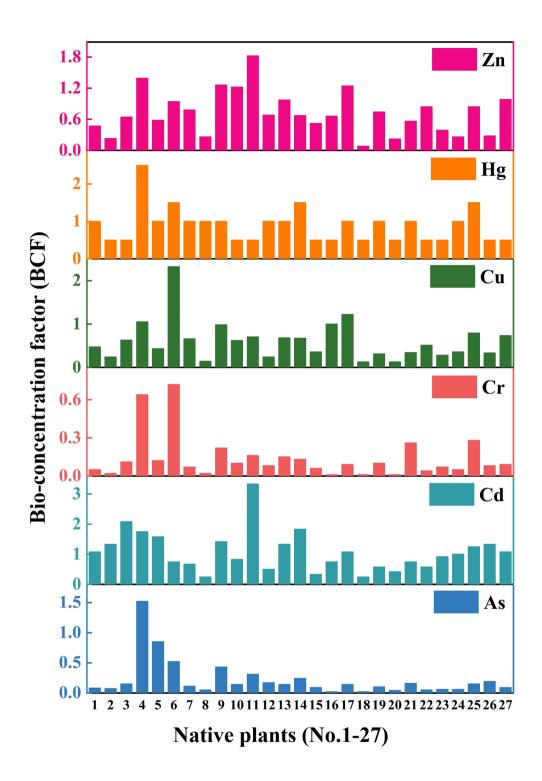


Fig. 6. Bioconcentration factor (BCF) of plants for heavy metals in the Yaojie Coal Mining Area.

or the heavy metals extracted from the plants to partially satisfy the demand for heavy metals. Moreover, other methods including physical engineering, chemical improvement and bioremediation should also be adopted for the integrated management of heavy metal pollution in the coal mining areas. Therefore, it is necessary in the future to analyze the concentration and form of heavy metals in the gangue, soil and plants (Includes above-ground and below-ground) around the Yaojie Coal Mine Area, combined with the analysis of rhizosphere soil physicochemical factors, to explore the transfer coefficient, accumulation pattern, influencing factors, migration mechanism and risk evaluation of heavy metals in the gangue-soil–plant system in the coal mine area, so that

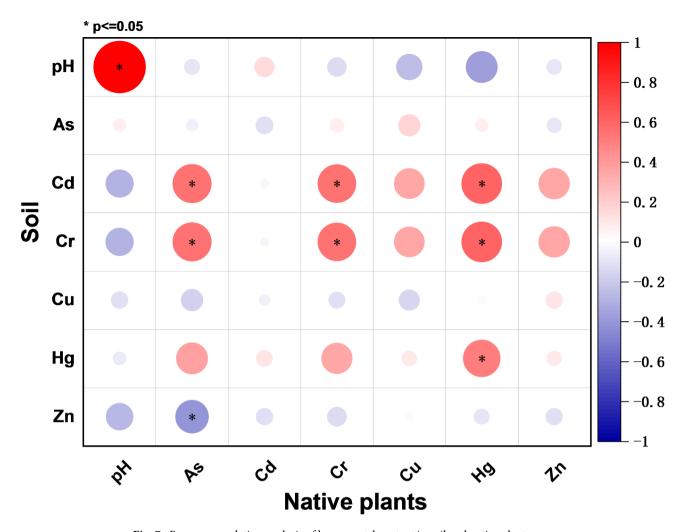


Fig. 7. Pearson correlation analysis of heavy metal content in soil and native plants.

we can provide a reliable basis for the evaluation of the ecological environment and the assessment of the risk to health in the study area.

Conclusion

In the study area, the Nemeiro comprehensive pollution index reaches 6.32, which was higher than the severe pollution level, where Hg being the most polluted (P = 8.50) and Cr, Cu, Zn being relatively clean. There are 6 different soil elements with varying coefficients of variation. Hg show strong variation with 105.8 (CV > 100%), that could be influenced by anthropogenic factors such as coal mining. Element concentration varied greatly in 27 native plants, the content in SK mine is generally higher than HSW mine. In the above-ground parts of 27 plants, metals exceeded the standard level except Zn, with the most severe exceedance being Hg in C. virgate was 19.2. The BCF of As and Hg were highest in the C. virgate, whereas Cr and Cu in X. sibiricum, Cd and Zn in S. glauca. Based on the findings in present work, C. virgata, X. sibiricum, and S. glauca are considered as promising candidates for multiple heavy metals remediation and can be used as potential pioneer species plants for phytoremediation of Yaojie Mining Area in GanSu in China. The results of this study consistent with our field sampling observations that these three species have high biomass and grow vigorously, as evidenced by a high tolerance to high concentrations of heavy metals. However, The soil quality in the area has exceed the Gansu Soil background value standard, and crops planting are not recommended. In fact, phytoremediation of coal mine wasteland can have much more diverse functions such as prevention of soil and wind erosion, nursery, providing habitat to wildlife, biodiversity conservation, etc., which can be used in conjunction with other restoration techniques such as chemical amendments for ecological restoration.

Data availability

The data that support the findings of this study are available from the corresponding author, [J. lu], upon reasonable request.

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Author contributions

All authors contributed to the study conception and design. Sample collection and analysis were performed by Juan Lu and Huiyu Wang. The draft of the manuscript was written by Juan Lu and Lei Gao commented on it for its improvement. All authors read and approved the manuscript.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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