

## Bioaccumulation of four metals in the same genus mosses (*Barbula* Hedw.) and soil pollution assessment in an abandoned karst bauxite tailing area

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**Abstract:** Soil metal pollution is a concern in bauxite tailing areas. This study aimed to effectively screen plants with strong tolerance to metal contamination by analyzing the levels of metals in *Barbula rigidula* (Hedw.) Mild. (BR), *Barbula indica* (Hook.) Spreng. (BI), and *Barbula vinealis* Brid. (BV) and in soils. The contents of metals in mosses obtained from the bauxite tailing area followed the following order: Al > Fe > Zn > Cu. Furthermore, the levels of these metals were highest in BR, followed by BI and BV. However, concentrations of Al (12,220–87,080 mg/kg), Fe (8520–62,690 mg/kg), Cu (98.5–185.4 mg/kg), and Zn (208.2–352.6 mg/kg) in soils greatly exceeded the background values. Bioconcentration factor (BCF) analysis showed that the uptake ability of mosses was 0.44–1.51, with BR having the highest uptake ability, especially for Al and Fe. The metal contamination factor (CF) in soils was 2.04–15.12, indicating that the soil was exposed to moderate to severe contamination. Correlation analyses found that Al and Fe levels in BR and soil were significantly positively correlated ( $r = 0.898$ ). PCA also confirmed that BR is a bioindicator and phytoremediation material of polluted soil in an abandoned karst bauxite tailing.

**Key words:** Bauxite tailing, mosses, bioaccumulation, soil contamination, assessment

### 1. Introduction

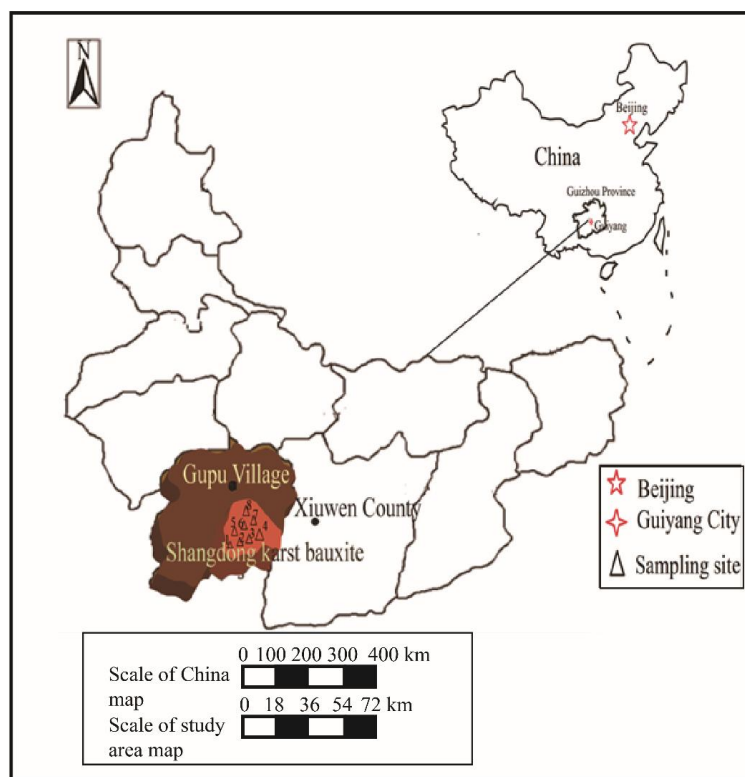
Bauxite is the world's main source of aluminum. Bauxite was discovered by geologist Pierre near the village of Les Baux in Provence, southern France (Berthier, 1821), but it was named "Bauxite" by Chemist Henri (Henri, 1861). Bauxites can be categorized into karst type and laterite type based on the bedrock lithology (Bárdosy et al., 1992). Most bauxites in China (95%) are karstic and widely spread within southwestern China and northern China (Deng et al., 2010; Wang et al., 2012; Liu et al., 2013). These karst bauxites were mainly formed during the carboniferous period as carbonate rocks (limestone or dolomite) formed via intense chemical weathering and residual accumulation of intercalated clay layers (Liu et al., 1999). Karst bauxite is a major bauxite resource in southwestern China.

Karst bauxite reserves in Guizhou Province account for about 17% of total reserves in China (Wen, 2004). Shangdong karst bauxite is an abandoned bauxite tailing area located in Xiuwen County, Guizhou Province, southwestern China (Figure 1). However, bauxite mining has caused soil metal pollution in this area. Furthermore, smelting emits metals, which are transferred to the surrounding crops, vegetables, water, and soil, which can enter human bodies through food chains or direct

ingestion, posing a serious hazard to human health. In addition, metal dust and particles produced during bauxite mining and processing can also affect human health (Zhang, 2000; Smirnov et al., 2004). The area became an abandoned bauxite tailing with only a few pioneer plants (mosses), herbaceous plants, and low shrubs (Figure 2). However, mosses are sensitive and tolerant to metals and thus have dominated the mining areas.

Therefore, mosses have been widely used for metal enrichment and monitoring analyses. Mosses can also be used as ecological indicators because they absorb and retain many metals via precipitation and dry deposition. Moreover, unlike other higher plants, mosses lack true roots or cuticle layers (Rühling et al., 1968). Mosses are sensitive to metal deposition (Markert, 1993). A previous study also showed that mosses could be used as a bioindicator of metal contamination (in mine areas) (Balabanova et al., 2017), atmospheric pollution (Onianwa, 2001; Marinova et al., 2010; Jiang et al., 2018), and soil/water pollution (Vazquez et al., 2004). Mosses can also monitor metal pollution in the bauxite mining area and respond to environmental factors (Wang et al., 2015; Long et al., 2016). The ecological distribution and gemmae diversity of mosses have also been investigated (Yin et

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**Figure 1.** Location of Shangdong abandoned karst bauxite tailing area in Xiuwen County, Guizhou Province, China. Showing the location of sampling sites 1–8.

al., 2014; Ji et al., 2015; Huang et al., 2017). However, the current studies only focused on revegetation of bauxite residues, ecotoxicological risk assessment, and microbial community colonization (Xue et al., 2016; Elisa et al., 2019, 2020a, 2020b; Macías-Pérez et al., 2022). Previous studies have also evaluated moss diversity, metal adsorption ability, and the microbial community of bauxite residues.

This is the first study to assess metal bioaccumulation and variation in the same genus mosses (*Barbula*) and soil pollution. This study aimed to: (a) determine the levels of four metal elements (Al, Fe, Cu, and Zn) in three mosses and soils, (b) explain how mosses absorb and accumulate high levels of metals, particularly Al and Fe, (c) analyze uptake ability of mosses and estimate soil pollution status, and (d) determine whether the same genus mosses (*Barbula*) can be used as ecoindicators of metal pollution and phytoremediation materials from an abandoned karst bauxite tailing via principal components analysis (PCA).

## 2. Materials and methods

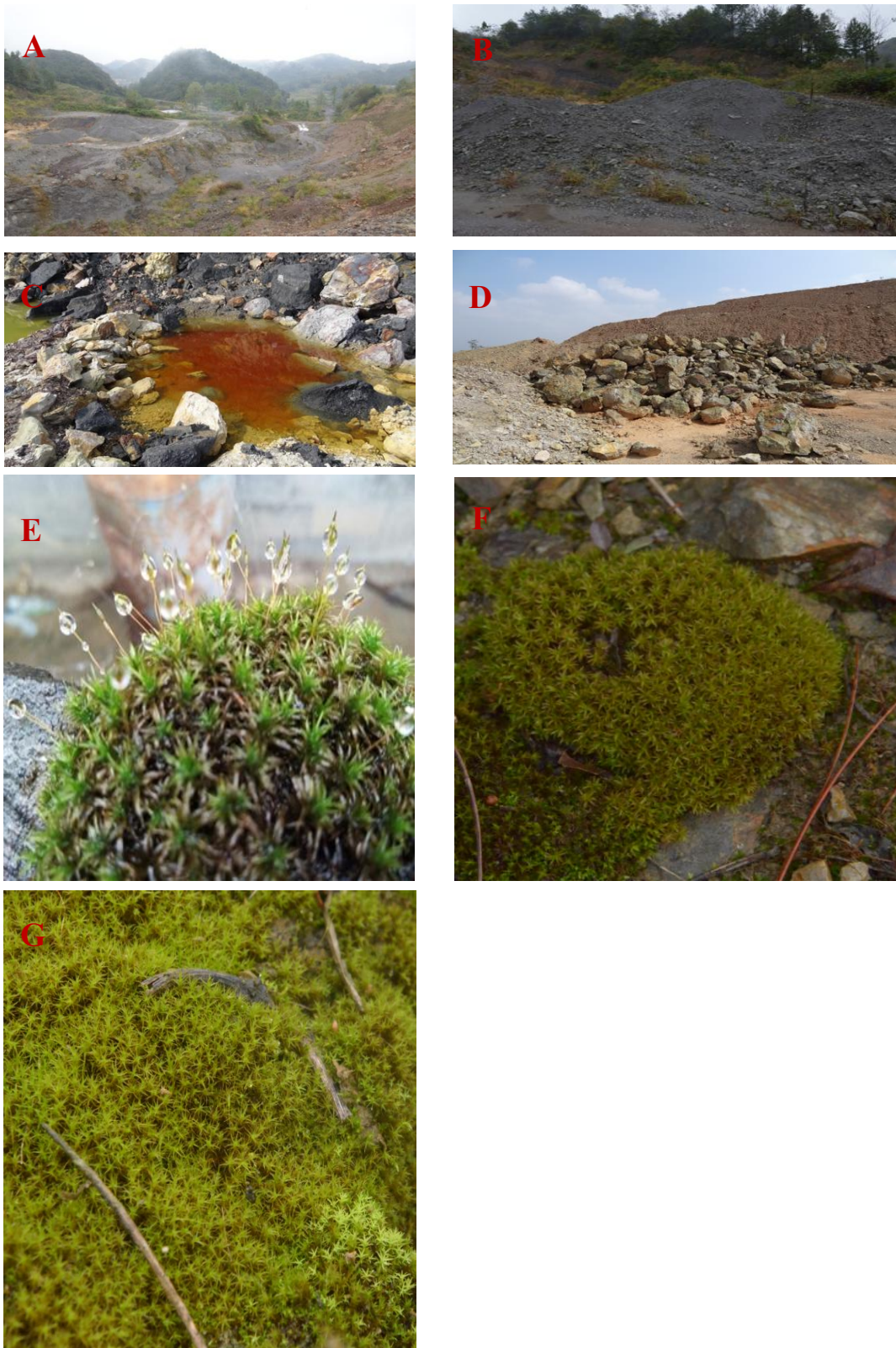
### 2.1. Study area

The abandoned Shangdong karst bauxite tailing area in the southwest of Xiuwen County, Guizhou Province, was selected as the study area (Figure 1). The region has many

complex karst landforms, such as karst peaks, caves, and karst depressions. The area experiences mild summers and winters with a mean annual temperature and mean annual precipitation of 13.6 °C and 1179.5 mm, respectively. The area has a forest cover of about 52%. The area has bauxite deposits formed via weathering of ancient lateritic sedimentary deposits, including  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{TiO}_2$  (Li et al., 2014a). This region has many waste rocks, waste residues, and vegetation (low shrubs, herbs, and dominant mosses) due to the early mining and smelting.

### 2.2. Sample collection and identification

Sampling was conducted in October 2021 from eight sampling sites at a depth of 1–2 cm (soil substrate underlying mosses). The soil in the area is thin, shallow, and of low fertility. Three to five samples were collected at each site within  $1 \times 1 \text{ m}^2$ . Moreover, 35 moss samples and their soil samples were collected within the eight sites. The moss samples were carefully packed into plastic bags and taken to the laboratory for species identification. Soil samples were placed in plastic bags and taken to the laboratory for further analysis. The mosses are shown in Table 1. *Barbula rigidula* (BR), *Barbula indica* (BI), and *Barbula vinealis* (BV) dominated the flora and were selected for analysis of metal content.



**Figure 2.** Environment and principal mosses on Shangdong abandoned karst bauxite tailing area. A. Karst bauxite tailing and residual vegetation; B. Waste residues pile area; C. Waste rocks pile area; D. Ore stockpile area; E. *Barbula rigidula* (Hedw.) Mild.; F. *Barbula indica* (Hook.) Spreng. and G. *Barbula vinealis* Brid. The same below.

**Table 1.** Mosses species, sample site distribution, and habitat of Shangdong abandoned karst bauxite tailing area.

| Family       | Genus              | Species  | Sample site        | Habitat   |
|--------------|--------------------|--|--------------------|---|
| Pottiaceae   | <i>Barbula</i>     | <i>B. rigidula</i> (Hedw.) Mild.                             | 1,2,3,4,7          | Waste residues and rocks, Low shrubs                                    |
|              |                    | <i>B. indica</i> (Hook.) Spreng.<br><i>B. vinealis</i> Brid. | 1,2,4,7<br>1,5,6,7 | Waste residues, Low shrubs and herbs<br>Waste residues and rocks, Herbs |
|              | <i>Hydrogonium</i> | <i>H. majusculum</i> (C. Muell.) Chen                        | 2,7                | Waste residues and ore, Low shrubs                                      |
|              |                    | <i>H. sordidum</i> (Besch.) Chen                             | 4                  | Waste rocks, Herbs  |
| Ditrichaceae | <i>Ditrichum</i>   | <i>D. brevidens</i> Nog.                                     | 2,6                | Waste residues and rocks, Herbs   |
| Bryaceae     | <i>Bryum</i>       | <i>B. argenteum</i> Hedw.                                    | 7,8                | Ore, Low shrubs and herbs   |

The moss species were identified using classical morphological and taxonomic identification methods, with reference to *Flora Bryophytarum Sinicorum* Vol. 1, 2 and Vol. 4 (Gao, 1994, 1996; Li, 2006), *Flora Yunnanica* Vol. 17 (Institutum Botanicum Kunmingense Academiae Sinicae Edita, 2000) and *Higher Plants of China in Colour* Vol. 1 (Zhang et al., 2016).

### 2.3. Sample preparation and chemical analysis

The moss or soil samples were oven-dried at 60 °C for 48 h, ground to a fine powder, and then sieved through a 100 (0.150 mm)-mesh sieve. Nitric acid (16 mL) and 4 mL of perchloric acid (for moss samples) or 12 mL of nitric acid and 3 mL of perchloric acid (HNO<sub>3</sub>:HClO<sub>4</sub> = 4:1) (for soil samples) were added to the samples (1 g for moss samples or 0.5 g for soil samples) before digestion in an electric furnace (Li et al., 2008; Wang et al., 2015). For soil samples only, HF (3 mL) was added to 0.5 g soil samples during digestion. The moss/soil samples were allowed to cool to room temperature after digestion and then transferred to 50-mL volumetric flasks. Distilled water was added to the samples to make the total volume of 50 mL. Three parallel and two blanks were prepared for further analysis (three replicates each) (Økland et al., 1999). Inductively coupled plasma mass spectrometry (ICP-MS) was used to assess the contents of Al, Fe, Cu, and Zn in moss and soil samples.

Quality assurance (QA) and quality control (QC) of metal analysis were assessed using duplicates, method blanks, and standard reference materials (SRM 2710, GBW 07404, and GBW 07602). The chemical analysis of the samples was conducted using common analytical methods. Data are expressed as mean of three replicates for each sample. Sensitivity (lower limit of detection) was also determined. Detection limits for the elements were analyzed using ICP-MS (10<sup>-4</sup> and 10<sup>-5</sup> ppm).

### 2.4. Data analyses

Bioconcentration factor (BCF) was used to evaluate the ratio of metal contents in mosses to that in soil for analysis of the enrichment ability. BCF can be used to measure bioaccumulation capacity, and thus can reveal the ability of

mosses to accumulate metals (Li et al., 2018; Ramachandra et al., 2018). BCF was calculated using equation (1) below:

$$BCF = \frac{C_{\text{mosses}}}{C_{\text{soil}}}, \quad (1)$$

where  $C_{\text{mosses}}$  and  $C_{\text{soil}}$  represent the metal concentration in mosses (mg/kg, dry weight) and corresponding element concentration in soil (mg/kg, dry weight), respectively.

The contamination level of each metal was determined using the contamination factor (CF), as shown in equation (2) below:

$$CF = \frac{C_{\text{soil}}}{C_{\text{background}}}, \quad (2)$$

where  $C_{\text{soil}}$  and  $C_{\text{background}}$  represent the corresponding element concentration in soil and soil metal background values for Guizhou Province, respectively. ( $CF < 1$ , none contaminated;  $1 < CF \leq 2$ , slightly contaminated;  $2 < CF \leq 3$ , moderate contamination;  $CF > 3$ , serious contamination) (Teng et al., 2002).

The correlations between metal concentrations in mosses and soils were determined using Pearson's correlation coefficients ( $r$ ) via Canoco for Windows 4.5. Principal components analysis (PCA) converts a set of observations of possibly correlated variables using an orthogonal transformation. KMO test (0.658) > 0.5 and Bartlett's test (sig. = 0.11) showed that the mosses/soils and metal concentrations were suitable for PCA (Yang et al., 2011; Li et al., 2014b).

## 3. Results and discussion

### 3.1. Mosses species composition characteristics

Bauxite mining in the Shangdong karst bauxite tailing area led to the destruction of native vegetation, leaving only some arid moss species. In this study, seven species, including Pottiaceae (*Barbula rigidula* (Hedw.) Mild., *Barbula indica* (Hook.) Spreng., *Barbula vinealis* Brid., *Hydrogonium majusculum* (C. Muell.) Chen and *Hydrogonium sordidum* (Besch.) Chen), Ditrichaceae (*Ditrichum brevidens* Nog.) and Bryaceae (*Bryum argenteum* Hedw.), belonging to

**Table 2.** Metal concentrations (mg/kg dry weight) of mosses and their soils, bioconcentration factor, and contamination factor.

|     | BR/SBR |        |       |       | BI/SBI |        |       |       | BV/SBV |      |       |       |
|-----|--------|--------|-------|-------|--------|--------|-------|-------|--------|------|-------|-------|
|     | Al     | Fe     | Cu    | Zn    | Al     | Fe     | Cu    | Zn    | Al     | Fe   | Cu    | Zn    |
| B   | 95,580 | 65,870 | 148.2 | 387.1 | 47,270 | 43,070 | 93.4  | 258.1 | 22,491 | 9635 | 72.7  | 207.4 |
|     | 87,080 | 62,690 | 185.4 | 352.6 | 36,830 | 53,000 | 170.8 | 254.6 | 15,417 | 9750 | 143.4 | 240.3 |
| BCF | 1.10   | 1.05   | 0.80  | 1.10  | 1.28   | 0.81   | 0.55  | 1.01  | 1.46   | 0.99 | 0.51  | 0.86  |
| CF  | 15.12  | 15.03  | 5.79  | 3.54  | 6.39   | 12.71  | 5.34  | 2.56  | 2.68   | 2.34 | 4.48  | 2.42  |
| C   | 34,830 | 45,430 | 86.2  | 236.3 | 22,030 | 18,750 | 84.7  | 206.5 | 17,132 | 8962 | 68.5  | 203.8 |
|     | 23,140 | 32,610 | 178.2 | 245.4 | 18,740 | 24,120 | 160.5 | 230.4 | 13,140 | 8730 | 110.2 | 213.6 |
| BCF | 1.51   | 1.39   | 0.48  | 0.96  | 1.18   | 0.78   | 0.53  | 0.90  | 1.30   | 1.03 | 0.62  | 0.95  |
| CF  | 4.02   | 7.82   | 5.57  | 2.47  | 3.25   | 5.78   | 5.02  | 2.32  | 2.28   | 2.09 | 3.44  | 2.15  |
| D   | 14,210 | 9764   | 68.8  | 212.4 | 12,720 | 8860   | 65.6  | 201.7 | 11,678 | 8454 | 64.5  | 200.2 |
|     | 15,580 | 18,250 | 154.7 | 232.6 | 14,130 | 13,110 | 120.7 | 210.8 | 12,220 | 8520 | 98.5  | 208.2 |
| BCF | 0.91   | 0.54   | 0.44  | 0.91  | 0.90   | 0.68   | 0.54  | 0.96  | 0.96   | 0.99 | 0.65  | 0.96  |
| CF  | 2.70   | 4.38   | 4.83  | 2.34  | 2.45   | 3.14   | 3.77  | 2.12  | 2.12   | 2.04 | 3.08  | 2.09  |
| SB  | 5760   | 4170   | 32    | 99.5  | 5760   | 4170   | 32    | 99.5  | 5760   | 4170 | 32    | 99.5  |

B. Waste residues pile area; C. Waste rocks pile area; D. Ore stockpile area. BR. *B. rigidula*; BI. *B. indica*; BV. *B. vinealis*. SBR. Soil substrate underlying BR; SBI. Soil substrate underlying BI; SBV. Soil substrate underlying BV. SB. Background values. BCF. Bioconcentration factor and CF. Contamination factor.

four genera and three families were identified in the area. These species adapted to the dry and metal-contaminated environment because of their physiological structure and characteristics. Species composition was monotonous, and all were turf mosses. The turf mosses could grow in arid and barren soil environment. However, *Barbula rigidula*, *Barbula indica*, and *Barbula vinealis* were the dominant species in the area, widely distributed in waste residues pile area, waste rocks pile area, and ore stockpile area.

Pottiaceae was the dominant family and included five species. Pottiaceae plants can survive under drought, high temperatures, destructive human activities, and mining area (study area) because of the long-term waste residues and sparse vegetation, which promote Pottiaceae species growth and distribution. In contrast, Brachytheciaceae and Hypnaceae are usually found in relatively humid locations, and grow well where there are less human activities and more vegetation cover (Giudice et al., 1997). However, the study area had sparse vegetation, and thus the growth of the mosses was inconsistent since the soil was thin, shallow, and had low fertility. Furthermore, the species richness was relatively low, probably due to waste residues and waste rock accumulation, low vegetation coverage, poor environment restoration, poor land reclamation, and poor green strategy. Therefore, vegetation restoration and environmental improvement can improve species richness.

### 3.2. Concentrations of metals in mosses

The concentrations of Al, Fe, Cu, and Zn in the three species are shown in Table 2. Total Al concentration was 11,678–95,580 mg/kg and was highest in *Barbula rigidula* (95,580 mg/kg) and lowest in *Barbula vinealis* (11,678 mg/kg). Furthermore, Al concentration was significantly higher in *Barbula rigidula* than in *Pteris vittata* L. root (24,750 mg/kg), probably due to the difference in Al absorption in the physiological structure of plants (Wang et al., 2020). These results indicate that plants in the same genus have different absorption abilities. Furthermore, total Al concentration was higher in *Barbula vinealis* than in aerial portion of *Bermudagrass* (Giridhar Babu et al., 2011). Results further found that mosses from different sites had different Al enrichment abilities, possibly due to the difference in bauxite mining and smelting degree (Long et al., 2016). Al content was highest in *Barbula rigidula* mainly due to the by-product of bauxite smelting. Meanwhile, Al content was also relatively higher in the soil. Moreover, Al concentration had the same pattern in other mosses at different gradients.

Furthermore, total Fe content was 8454–65,870 mg/kg and was highest in *Barbula rigidula* (65,870 mg/kg) and lowest in *Barbula vinealis* (8454 mg/kg). The high Fe levels in *Barbula rigidula* was related to the waste residues produced during mining activities. Furthermore, Fe content was significantly higher in *Barbula rigidula* than in

*Hydrogonium gangeticum* (C. Muell.) Chen, due to regional difference (Long et al., 2016). Also, Fe content was higher in *Barbula vinealis* than in aerial portion of *Bermudagrass*, indicating that the moss could easily adsorb Fe (Giridhar Babu et al., 2011).

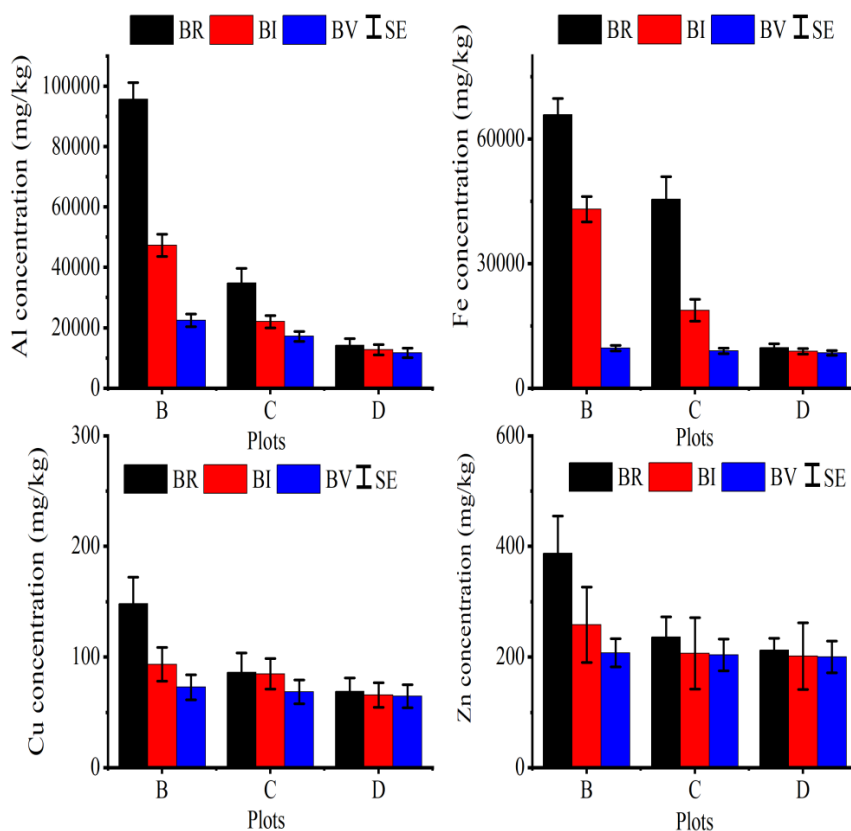
The concentrations of Cu and Zn were relatively low, ranging from 64.5 to 387.1 mg/kg. The levels of Cu and Zn were highest in *B. rigidula* (148.2 mg/kg and 387.1 mg/kg, respectively), possibly due to tail gas and the dust generated during the transportation after mining and smelting activities. The contents of Cu and Zn were lowest in *B. vinealis* (64.5 mg/kg and 200.2 mg/kg, respectively). Furthermore, Cu content was higher in *B. vinealis* than in *Hypnum cupressiforme* Hedw., possibly due to ecophysiological structure. Meanwhile, Zn contents were lower in the three mosses than in *Hypnum cupressiforme*, indicating that various mosses have different absorption abilities in different mines (Balabanova et al., 2017).

Furthermore, *B. rigidula* (BR) had higher bioaccumulative ability than other species (Figure 3). Concentrations of Al, Fe, Cu, and Zn decreased in the following order: *B. rigidula* > *B. indica* > *B. vinealis*. *B. rigidula* could tolerate and accumulate high levels of

metals, particularly Al and Fe. The metal contents in mosses had the same pattern at different gradients. The moss plants were distributed in the waste residues pile area, waste rocks pile area, and ore stockpile area of karst bauxite mine area, where some pioneer plants can grow. These results indicate that the mosses can be used as ecological indicators, especially *B. rigidula*.

### 3.3. Concentrations of metals in soil

The total concentrations of Al, Fe, Cu, and Zn in soils are shown in Table 2. Total Al content in the soil was 12,220–87,080 mg/kg and was highest in soil substrate with *B. rigidula* species (87,080 mg/kg) and lowest in soil substrate with *B. vinealis* species (12,220 mg/kg). The high Al content in soil substrate with *B. rigidula* species was related to waste residues generated during aluminum ore smelting and rainwater leaching. Furthermore, the total Al contents were lower in soil substrate with *B. rigidula* species than in the soil sample of bauxite waste residues pile (97,300 mg/kg), possibly because of the regional differences (Long et al., 2016). Nonetheless, total Al content was higher in soil substrate with *B. rigidula* species than in rhizosphere soils of six vascular plants (Wang et al., 2020). In addition, the concentration of total Al was higher in soil substrate with



**Figure 3.** Metal concentrations of three mosses species from the Shangdong abandoned karst bauxite tailing area. B, C, D: Different gradients. SE: Standard error.

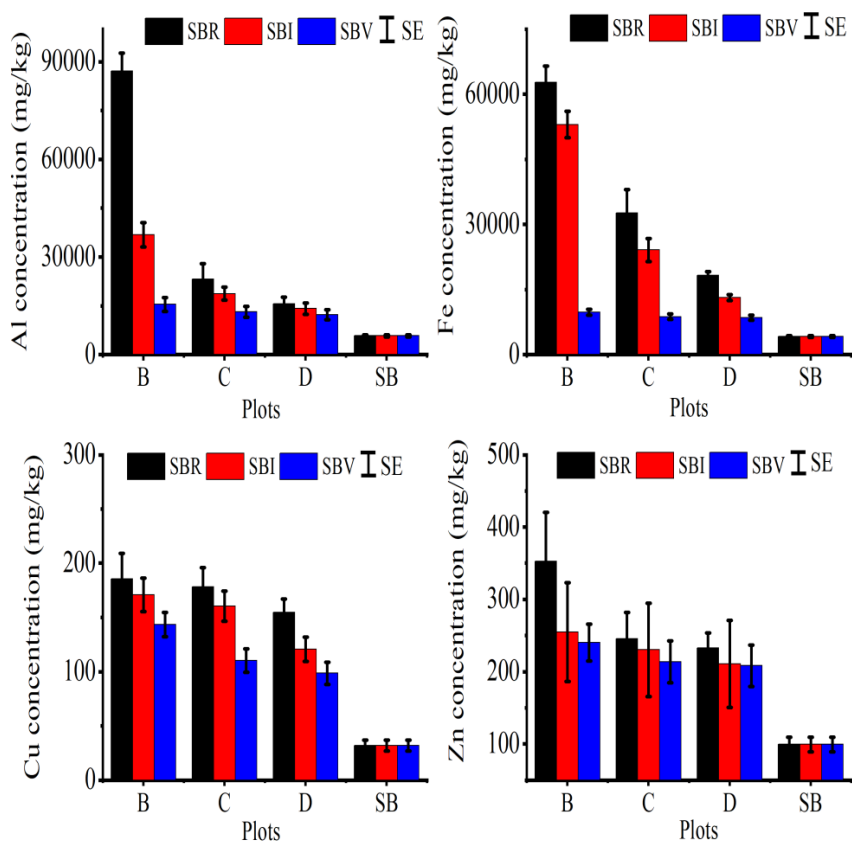
*B. vinealis* species than in topsoil of *Bermudagrass* (776 mg/kg), possibly due to soil type differences (Giridhar Babu et al., 2011). Furthermore, Al concentrations of the soils were significantly higher than the background levels (Jia et al., 2014; National Environmental Monitoring Station, 1990). These results further show that the soil was polluted with aluminum metal. Al content in soil substrates decreased in the following order: soil substrate underlying BR (SBR) > soil substrate underlying BI (SBI) > soil substrate underlying BV (SBV).

Fe concentrations in the soil samples ranged from 8520 to 62,690 mg/kg and were highest in soil substrate with *B. rigidula* (62,690 mg/kg) and lowest in soil substrate with *B. vinealis* species (8520 mg/kg). The high Fe level was mainly related to waste residues produced by smelting activities. Furthermore, Fe content was higher in soil substrate with *B. vinealis* species than in topsoil of *Bermudagrass* (Giridhar Babu et al., 2011). Total Fe content in soil substrate with *B. rigidula* and soil substrate with *Hydrogonium gangeticum* (62,900 mg/kg) was similar (Long et al., 2016). Besides, Fe concentration was higher in soil substrates than the background level for Guizhou Province, showing that the soil was contaminated by iron. Similarly, Fe contents in the

soils decreased as follows: SBR > SBI > SBV.

Concentrations of Cu and Zn in soil substrates were relatively low, ranging from 98.5 to 352.6 mg/kg. Cu and Zn contents were highest in waste residues pile area, (185.4 mg/kg and 352.6 mg/kg, respectively) (soil with *B. rigidula*) and lowest in the soil with *B. vinealis* (98.5 mg/kg and 208.2 mg/kg, respectively). Cu content was higher in the soil with *B. vinealis* than in soil with orchards near bauxite mine (60.4 mg/kg), possibly due to soil type differences. Meanwhile, Zn content was lower in soil substrates than in the aluminum mill area (755.1 mg/kg) (Wang et al., 2015). Cu and Zn contents in soil were mainly due to rainwater leaching. Moreover, Cu and Zn contents were higher in soil substrates than the background levels, showing that the soil was contaminated with Cu and Zn. The concentrations of Cu and Zn in soil substrates decreased as follows: SBR > SBI > SBV.

Metal concentrations were different in the various soil substrates (Figure 4). The concentrations of Al, Fe, Cu, and Zn in the soil samples decreased as follows: SBR > SBI > SBV. The metal contents in the soil samples had the same pattern at different gradients. Furthermore, metal concentrations in soil substrates were higher than the



**Figure 4.** The metal concentrations of soil substrates underlying mosses from the Shangdong abandoned karst bauxite tailing area. SB: Background values.

background levels, showing that the soil was contaminated. However, metal contents were higher in the soil substrates with *B. rigidula*, especially Al and Fe, and thus can be used to indicate soil metal contamination.

### 3.4. Bioaccumulation characteristics and soil assessment

The mosses had different bioaccumulation capacities with a BCF ranging from 0.44 to 1.51 (Table 2). *B. rigidula* from waste rocks pile area had the highest bioaccumulation capacity (Al), while *B. rigidula* from ore stockpile area had the lowest bioaccumulation capacity (Cu).

The enrichment ability of the mosses was different at various gradients based on the BCF of Al and Fe metals. The BCF of Al in the mosses was >1, except for ore stockpile area, (maximum value; 1.51), indicating that the mosses contained Al and the soil was moderately polluted. Similarly, Fe enrichment capacity of the mosses was different. Fe had the highest BCF in *B. rigidula* (1.39), indicating that *B. rigidula* contained much Fe metal and the soil was moderately contaminated. BCF of Fe in *B. rigidula* in ore stockpile area was the lowest (0.54).

The Cu enrichment capacity of the mosses was also different at various gradients. However, BCF of Cu was relatively low (BCF < 1), indicating that the soil was relatively depleted. The enrichment capacity of Cu was highest in *B. rigidula* in waste residues pile area (0.80) and lowest (0.44) in *B. rigidula* in ore stockpile area. Moreover, BCF of Zn in *B. rigidula* and *B. indica* in waste residues pile area was relatively higher (BCF > 1) than in *B. vinealis* (BCF < 1) at different gradients.

Furthermore, the contamination level of each metal was significantly different (Table 2). Contamination factor (CF) of metals in the soil samples ranged from 2.04 to 15.12. The CF of Al in the soil substrate with *B. rigidula* was the highest (CF:15.12), indicating that the soil was severely contaminated. The CF of Fe in the soil substrate with *B. vinealis* was the smallest (2.04), indicating that the soil was moderately contaminated. Metal contamination

can lead to moderate to severe contamination in the soil. The CF of the four metals (especially Al and Fe) in the soil substrates with *B. rigidula* was > 3.54 (in waste residues pile area), indicating that the soil was severely contaminated. The CF of Cu in the soil substrate ranged from 3.08 to 5.79, indicating that the soil was severely contaminated. The CF of Zn in soil substrate ranged from 2.09 to 3.54, showing that the soil was polluted. In summary, the CF of four metals was highest in the soil substrate with *B. rigidula* and lowest in the soil substrate with the other two mosses. However, the soils were exposed to different contamination risks.

### 3.5. Correlation analysis of metal contents in mosses and soil

The correlation analyses between metal concentrations in mosses and soils are shown in Table 3. Al and Fe contents were significantly positively correlated ( $r = 0.898$ ). Al and Zn contents were significantly positively correlated ( $r = 0.962$ ). Fe and Zn contents were significantly positively correlated ( $r = 0.867$ ). Cu and Zn contents were significantly positively correlated ( $r = 0.606$ ). Fe and Cu contents were significantly positively correlated ( $r = 0.580$ ). However, Al and Cu contents were not correlated. These results indicate that there may be a synergistic effect among the contents of the metals (Al, Fe, Cu, and Zn) in mosses and their soils except for Al and Cu. A study also showed that Al and Fe contents in different mosses of karst bauxite are correlated (Long et al., 2016). Al and Fe contents were highest in *B. rigidula* and their soils, confirming that *B. rigidula* had high tolerance and sensitivity to these metals. Therefore, *B. rigidula* can be used to assess metal tolerance and sensitivity in plants. Furthermore, *B. rigidula* can be used to determine species that can grow in polluted soil.

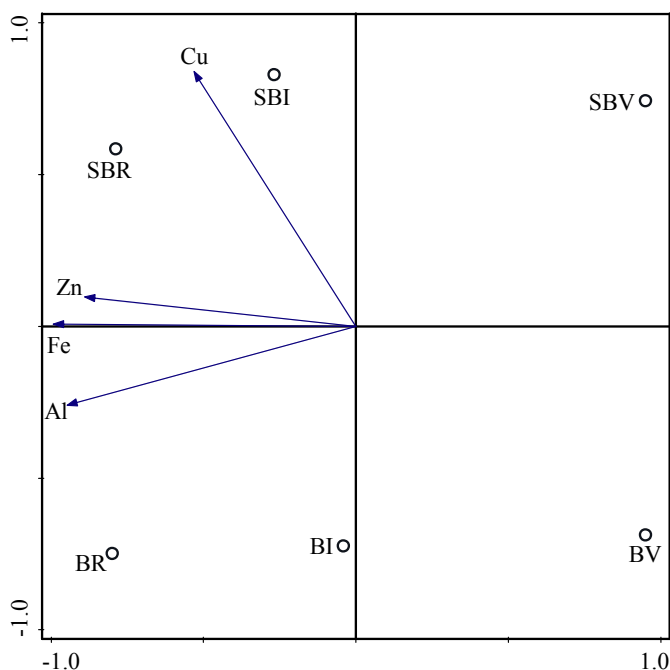
Eigenvalues and explained variation are shown in the PCA diagram (Figure 5) (Table 4). The metal concentrations in the three mosses and their soils were relatively high and positively correlated, especially

**Table 3.** Correlation analysis between metal concentrations in mosses and their soils.

|    | Al | Fe                 | Cu                 | Zn                 |
|----|----|--------------------|--------------------|--------------------|
| Al | 1  | 0.898 <sup>a</sup> | 0.447              | 0.962 <sup>a</sup> |
|    |    | 0.000              | 0.063              | 0.000              |
| Fe |    | 1                  | 0.580 <sup>b</sup> | 0.867 <sup>a</sup> |
|    |    |                    | 0.012              | 0.000              |
| Cu |    |                    | 1                  | 0.606 <sup>a</sup> |
|    |    |                    |                    | 0.008              |
| Zn |    |                    |                    | 1                  |

<sup>a</sup>Significant positive correlation ( $p < 0.01$ ); <sup>b</sup>Significant positive correlation ( $p < 0.05$ ).





**Figure 5.** Principal component analysis of metal concentrations in mosses and in underlying soils on an abandoned karst bauxite tailing area.

**Table 4.** Eigenvalues and explained variation of principal component analysis.

|                     | Axis 1 | Axis 2 | Axis 3 | Axis 4 |
|---------------------|--------|--------|--------|--------|
| Eigenvalues         | 0.8556 | 0.1215 | 0.0221 | 0.0008 |
| Explained variation | 85.56  | 97.71  | 99.92  | 100.00 |

between the *B. rigidula* species and their soil. Al and Fe levels were highest in *B. rigidula* and their soil and were correlated (BR, SBR). Cu and Zn contents were low in the three mosses species and their soil, especially in the *B. vinealis* and their soil. Furthermore, Al, Fe, Cu, and Zn concentrations in the mosses decreased in the following order: BR > BI > BV. The same pattern was found in their soils. These results were consistent with the measured values. However, Al, Fe, Cu, and Zn contents were higher in soils than the background level, showing that soil was moderately contaminated to severely contaminated.

PCA revealed that metal concentrations were different in the mosses and soils, possibly because of ore smelting activities and human activities. The three mosses had good absorption capacity, especially *B. rigidula*. PCA confirmed that *B. rigidula* adapted to the abandoned karst bauxite environment and could tolerate and accumulate metals, particularly Al and Fe. A previous study found that mosses with high tolerance to metals

can be used to assess contaminated environments (Shaw, 1994). Meanwhile, *B. rigidula* also had strong absorption ability and thus can be used as a key ecological index to assess. Therefore, this study can provide insights into land reclamation, green strategy, and vegetation restoration.

#### 4. Conclusion

In this study, seven species belonging to four genera and three families of mosses were detected in the abandoned Shangdong karst bauxite tailing area, of which *Barbula rigidula*, *Barbula indica*, and *Barbula vinealis* were the dominant species. Species composition was monotonous, and all were turf mosses due to waste residues and waste rock accumulation, and low vegetation coverage.

The concentrations of Al, Fe, Cu, and Zn in mosses decreased in the following order: *B. rigidula* > *B. indica* > *B. vinealis*. The contents of the soil samples showed the same pattern in different gradients: SBR > SBI > SBV. Levels of Al, Fe, Cu, and Zn in *B. rigidula* and their

corresponding soils were relatively high, especially Al and Fe, and thus can be used as indicators of soil metals contamination.

Bioconcentration factor (BCF) analysis showed that the bioaccumulation of the four metals in mosses showed different levels, ranging from 0.44 to 1.51. BCF of Al and Fe metals in *B. rigidula* was the largest, being 1.51 and 1.39, respectively. There were significant differences in the contamination level of each metal. Contamination factor (CF) of metals in the soil samples ranged from 2.04 to 15.12. Thus, soils were exposed to moderate to serious contamination.

Correlation analyses suggested that there may be synergistic effects among the three metals (Al, Fe, and Zn) in mosses and their soils. Al and Fe were significantly positively correlated ( $r = 0.898$ ) in *B. rigidula* and their soil. Levels of Al and Fe were highest in *B. rigidula* and their soil and showed good correlation. PCA results confirmed that *B. rigidula* was well adapted to the karst bauxite environment and had a strong ability to absorb metals, which may be used as an important ecological index to metals pollution. As a result, *B. rigidula* was reported to be an important pioneer plant indicator of metals pollution, which was also a valuable phytoremediation material for mine land reclamation, green strategy, and revegetation.

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## Competing interests

No conflicts of interest exists in the submission of this manuscript, and the manuscript has been approved by all authors for publication. No financial competing interests exist in this study.

## Ethical statement

All the authors declare that the work described was original research that has not been published previously. This study does not violate the code of ethics and conduct. All the authors listed have approved the enclosed manuscript.

## Author contributions

ZHZ designed the study. DFW wrote the manuscript. QMW finalized the figures and tables and carried out the experiments. All the authors have read and approved the manuscript.

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