Phytoremediation Potential of Indigenous Plants Growing at Nchanga Mine in Chingola, Zambia

Lupupa Kachenga*, Harry Nixon Chabwela, Kasuka Mwauluka

Department of Biological Sciences, University of Zambia, Lusaka, Zambia
Email: tembolk@gmail.com

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Abstract

Mining and smelting processes are among the key sources of soil contamination by heavy metals resulting in dramatic disturbances and loss of biodiversity. Native plants growing naturally in hostile mining environments can be used for management, decontamination and possible rehabilitation of polluted soils. These plants are either excluders or accumulators based on their Bioaccumulation Factors (BAF). This, therefore requires identification of native plants that are able to accumulate heavy metals in their plant tissues at concentrations higher than that in the soil in which they are growing. This study investigated the phytoremediation potential of indigenous plants growing at the tailings dams of Nchanga Mine in Chingola, Zambia. TD4 and a site 50 m away from TD4 were sampled as Sampling Areas One (1) and Two (2), respectively. TD4 was divided into four quadrants and three plots from each quadrant were randomly sampled. Three plots from each of the two quadrants from Sampling Area Two were also sampled. Composite soil samples were collected from the plots and a total of 175 individuals of 16 grass and herbaceous plant species were collected and analysed. Atomic Absorption Spectrophotometry was used to determine the concentrations of Copper (Cu) and Zinc (Zn) in the soils and plant specimens. The findings of the study showed that the concentrations of Cu and Zn in the soil ranged from 891.41 mg/kg to 15,617.47 mg/kg and 20.73 mg/kg to 96.85 mg/kg, respectively. Arthraxonquartinianus had the highest concentration of Cu (1016.8 mg/kg) while Cyperusrotundus had the lowest (29.35 mg/kg). Arthraxonquartinianus had the highest concentration of Zn (192.8 mg/kg) and Crinum had the lowest (28.24 mg/kg). BAF values for Cu were less than 1 in all the plants and BAF values for Zn were highest in Arthraxonquartinianus (10.77) with Crinum having the lowest BAF of 0.01. The Bioaccumulation Factors indicated that all the plant species studied were Cu excluders; and with
the exception of *Crinum*, all were Zn accumulators and *Arthraxonquartianus*, a hyperaccumulator of Zn.

**Keywords**

Accumulators, Excluders, Indigenous Plants, Phytoremediation

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1. Introduction

The mining industry is the backbone of Zambia’s economy making up 80% of foreign earnings [1]. A large proportion of the world’s minerals come from developing countries such as Brazil, China, including Zambia. However, mining is one of the anthropogenic activities causing some of the most dramatic disturbances on biodiversity, water quality, and land use [2]. Increased mining activity increases the amount of degraded land. The degraded land includes bare stripped areas, loose soil piles, waste rock and overburden surfaces and subsided land areas. Surface mining or open pit mining causes up to 11 times more land destruction compared to underground mining; fertile land is transferred into wasteland or bog and local status of water and landscape deteriorates with some ecosystems being entirely destroyed [3] [4].

Mining and smelting processes are among the key sources of heavy metal contamination of soil and water [5]. Although many metals are essential, all metals are toxic at a high concentration due to the oxidative stress that they cause by formation of free radicals, as well as disrupting the function of pigments and enzymes [6]. As a result, soil contaminated with heavy metals is rendered unsuitable for plant growth, thereby resulting in the loss of biodiversity [7].

In the recent past, there has been increasing concern for the environment and as such, post-mining reclamation of degraded land should be an integral feature of the mining spectrum [2]. Reclamation is the process by which highly degraded land is returned to productivity and some measure of biotic function and productivity is restored [8]. There are a number of methods that have been used to cope with the soil pollution of degraded lands. Current techniques include excavation, chemical stabilization, soil washing or soil flushing [9], but these methods are sophisticated techniques and are suitable for relatively small soil volumes at sites that require immediate action [6] [9]. They are costly, time consuming and sometimes environmentally destructive rendering the soil unusable after treatment [10] [11].

In recent years, there are cost effective technologies that have been generated by scientists and engineers. These include the use of microorganisms/biomass or live plants to clean up the polluted areas and phytoremediation.

Phytoremediation is an emerging cost effective technology that has aesthetic advantages and long term applicability [12] [13]. Phytoremediation is an integrated multidisciplinary approach and involves the efficient use of plants to
eliminate, detoxify or immobilize environmental contaminants that are present in a growth matrix such as soil, water or sediments, through the natural, biological, chemical or physical processes of the plants [12]. The vegetation is capable of improving the nutrient conditions of the soil thereby setting the base for establishment of self-sustaining vegetation cover [14].

Metal tolerant plants are able to grow in contaminated soils as they have evolved mechanisms to minimize the effects of exposure to heavy metals [15]. Plants that are able to take up heavy metals to a greater concentration than that in the soil in which it is growing are called Hyperaccumulator plants [16] [17]. Hyperaccumulators that grow in polluted areas can accumulate large concentrations of heavy metals in their shoots; consequently, the removal of metals from the soil can be enhanced considerably by the judicious selection of plant species [18]. Some plants are excluders, meaning, they restrict the transport of heavy metals to the shoot and maintain relatively low concentrations of heavy metals [15]. Therefore, it is important to search for plants that spontaneously colonize these disturbed sites [9]. Research has shown that native plants growing naturally in hostile mining environments are potential phytoremediators and can be used to rehabilitate the disturbed sites [19]. Identification of indigenous hyperaccumulator plants is therefore imperative for the successful implementation of phytoremediation for mine reclamation mainly because native plant species require less management and they are acclimatized to the native climatic conditions and seasonal cycle [20] [21] [22].

Most Cu and Zn hyperaccumulator plants that have been identified are specific to Europe, Asia, the USA, and other African Countries like Congo DR and Zimbabwe. However, few species of Zambian native vegetation have been identified, namely, Cheilanthesperlanata, Eragrostisracemosa, Bulbostylispseudoperennis, Aspilia ciliate, Conyzacordat, Persicariapuncataand Persicariacapitata [23] [24].

The general objective of this study was to assess the phytoremediation potential of indigenous plants growing at the Nchanga Mine Tailings in Chingola, Zambia.

The hypotheses being tested in the study were: that the plants growing at the study site at Nchanga Mine had no potential for phytoremediation of Cu and Zn and that there was no relationship between the concentrations of Cu and Zn in the soil and in the plant species growing at the study site.

2. Materials and Methods

2.1. Study Area

The study was conducted at Nchanga Mine in Chingola. Chingola is a town in the Copperbelt Province of Zambia. It is situated at an elevation of 1340 meters above sea level on the Central African Plateau, 12˚ 30’S latitude, 27˚ 50’E Longitude [25]. Nchanga Mine which has the largest Open Pit Mine in Africa is operated by Konkola Copper Mines (KCM) Plc. The mine workings lie in an arc
which is 11 km long around the west and north of the town (Figure 1), covering nearly 30 km² [26], as such, the extent of the land degradation and soil contamination by heavy metals is of serious concern.

2.2. Sampling and Analysis

2.2.1. Plant and Soil Sampling

A stratified random sampling approach was used. Two sampling areas were established; one at the Tailings Dam four (TD4) (Figure 1) as sampling Area one (01) and the other covering the immediate vicinity of the tailings impoundment which served as the control site. Each sampling area was divided into four quadrats using a compass. In each quadrat, nine (9) 10 m × 10 m plots were established and three were randomly picked and sampled.

For each plant species present in each plot, at least three individuals were collected. The plant specimens were tagged, put in a polythene bag and placed in a cooler box. The plant specimens were identified using taxonomic keys and unidentified specimens were pressed and identified using voucher specimen in the University of Zambia Herbarium.

A soil probe was used to collect soil samples at depths of 15 - 20 cm. Three soil samples were collected in each plot at different points. A composite sample from each plot was then obtained by mixing the three samples well. The composite samples were placed in labelled polythene bags and stored in airtight containers.

2.2.2. Plant Diversity Study

A line transect was laid in each quadrat, running north to south. A square 1 m × 1 m grid was used to record the plant species present and the number of individuals. The grid was placed along the transect every two meters and the species present in the grid were recorded.

2.2.3. Quantitative Analysis

The important quantitative analysis such as density, frequency, and abundance

Figure 1. Map showing location of Nchanga open pit mine workings and TD4 (Google earth).
of the herbs and grass species were determined according to Curtis and McIntosh [27]. The Species richness was calculated using the method “Margalef’s index of richness” $D_{mg}$ [28]. The species diversity was computed using the Shannon-Wiener Index ($H'$) [28].

2.2.4. Chemical Analysis of the Soil Samples
The soil samples were air dried in the laboratory at room temperature by spreading them out on transparent plastic for seven days. The samples were then passed through a 2 mm sieve and ashed in porcelain crucibles in a furnace at 450˚C for three hours. Acids used in the extraction of the heavy metals were all Analytical Grade. One gram of each of the soil samples was placed in a 200 mL conical flask, to which 0.2 mL of sulfuric acid. 1 mL Nitric acid and 5 mL of perchloric acid were added too. The mixture was then placed on a hotplate and heated to 180˚C for 15 minutes. The mixture was allowed to cool and then filtered through Whatman No. 42 filter paper into 100 mL volumetric flasks. Distilled water was added to the mark. The filtrate was then transferred to 100 mL plastic bottles.

The concentrations of the Cu and Zn were determined using an Atomic Absorption Spectrophotometer (AAS), Analyst™ 900 (Perkin Elmer Instrument, USA) with an acetylene flame. The concentration of the heavy metals were calculated in mg/kg dry weight.

2.2.5. Chemical Analysis of the Plant Samples
Plant samples were dusted with a light brush and then dried at room temperature in the laboratory for one week. They were then placed in an electric steel oven for at least three hours at 110˚C before being ground using a steel grinding mill. 3 g of each of the ground and dried samples were then ashed in a controllable muffle furnace at 450˚C. the resulting ash was dissolved in 20 ml of 1 M analytical grade nitric acid and the solution was evaporated to near dryness. The samples were then filtered through ashless Whatman filter paper into 100 cm³ volumetric flasks. The residue on the filter paper was washed several times with distilled deionised water. The resulting filtrate was diluted to the mark using distilled deionised water. The concentrations of Cu and Zn were then determined using an Atomic Absorption Spectrophotometer, as in the soil samples above.

2.2.6. Analysis of Phytoremediation Potential
The phytoremediation potential was assessed by calculating the bioaccumulation factor (BAF).

$$BAF_{shoot} = \frac{c_{\text{shoot}}}{c_{\text{soil}}}$$

where $c_{\text{shoot}}$ is the metal concentration in the shoots and $c_{\text{soil}}$ is the metal concentration in the soil [29].

Plants that have a BAF shoot value greater than one are accumulators, whereas, plants that have BAF shoot values less than one are considered excluders [15] [29].
3. Results and Discussion

3.1. Concentrations of Cu (mg/kg) and Zn (mg/kg) in the Soil

The study site was characterized by high concentrations of Cu and Zn as was expected, considering the fact that the study site was located in the mine area, and at an old tailings dump to be precise. The Cu and Zn concentrations in the soil ranged from 2342.04 mg/kg to 12,024.49 mg/kg and 24.22 mg/kg to 67.99 mg/kg respectively (Table 1). The quadrats in TD4 had some of the highest values, compared to quadrats in the control site, 50 m away from TD4. The results showed that the soil had very high concentrations of Cu, much higher than the threshold value of 20 mg/kg according to WHO [30] and 130 mg/kg, according to ICRCL [31]. The concentrations of Zn were higher than the permissible values of 40 mg/kg according to WHO [30], but below the threshold value of 300 mg/kg according to ICRCL [31].

Soils from S1 had the highest concentration of Cu (12,024.49 mg/kg), followed by W1 (5700.45 mg/kg) and N1 (5364.67 mg/kg). With regards to Zn, S1 had the highest concentration (67.99 mg/kg) followed by N1 (34.05 mg/kg) and E1 (32.44 mg/kg). The difference in the concentrations of Cu and Zn in the quadrats in TD4 can be attributed to the direction of flow of the tailings discharged into the tailings dump. The flow is from north to south, with the most tailings settling on the southern part of the tailings dump. The dump is in such a way that it slants to the south. The high concentrations in the immediate vicinity of the tailings dump, 50 m away had Zn and Cu concentrations which were ranging from 2343.04 mg/kg to 4381.25 mg/kg, which however, lower than TD4, are still higher than recommended values. This may be due to waste rock, leachate from mine tailings and deposition of wind-blown particulates from piles [32].

3.2. Concentrations of Cu and Zn in the Plants Growing at TD4

A total of 175 individuals of 16 plant species were collected and analyzed for heavy metals. According to WHO [30], the maximum acceptable values of Cu and Zn in plants is 10 mg/kg and 50 mg/kg, respectively. The Zn content of plants in this study was ranging from 26.47 mg/kg to 174.32 mg/kg, with

| Sampling Area | Mean | SE of Mean | Median | Range | Mean | SE of Mean | Median | Range |
|---------------|------|------------|--------|-------|------|------------|--------|-------|
| TD4           |      |            |        |       |      |            |        |       |
| N1            | 5364.67 | 349.36      | 6042.54 | 1042.06 - 6720.92 | 34.05 | 0.65     | 32.35 | 27.58 - 37.94 |
| E1            | 4943.95 | 153.79      | 4737.41 | 3857.34 - 6023.37 | 32.44 | 0.58     | 31.66 | 27.59 - 36.34 |
| S1            | 12024.49 | 455.95     | 12397.77 | 8925.36 - 15,617.47 | 67.99 | 4.11     | 59.74 | 42.91 - 96.85 |
| W1            | 5700.45 | 99.53      | 5857.67 | 5196.85 - 6214.71 | 30.41 | 0.73     | 30.90 | 25.84 - 33.46 |
| Site 50 m away from TD4 |      |            |        |       |      |            |        |       |
| N2            | 2342.04 | 401.24      | 1813.80 | 891.41 - 5112.44 | 24.22 | 0.86     | 23.59 | 20.73 - 29.99 |
| W2            | 4381.25 | 350.12      | 3900.72 | 2403.52 - 6251.75 | 28.85 | 0.34     | 29.69 | 26.99 - 30.84 |

Table 1. Mean concentrations of Cu and Zn in the soil cover and Tailings at TD4 and the site 50 m away from TD4.
Digitariaeriantha, cornyzacordata and Arthraxonquartinianus having higher values. Plant species with some of the high values of Cu concentration recorded included Arthraxonquartinianus (1016.8 mg/kg), Digitariaeriantha (1282.2 mg/kg) and Vernonia (588 mg/kg) (Table 2). Cu content in plants was lowest in Cyperusrotundus (20.99 mg/kg) and Crinum (50.2 mg/kg). The concentration of Zinc in the plants (Table 3) was mostly above the recommended values according to WHO [30], but below the threshold value of 300 mg/kg according to ICRCL [31].

3.3. Correlation between Soil Metal Concentration and Plant Metal Concentration

Table 4 and Table 5 show the correlation coefficient between soil Cu and Zn concentration and the concentration of Zn and Cu in the plant species. The correlation between Cu concentration in the soil and Cu concentration in the plant species is 0.376, whereas, the correlation between concentration of Zn in the soil and concentration of Zn in the plant species is 0.359. The correlation coefficient is weak, but positive. This shows that there is a positive relationship between the concentration of Cu and Zn in the soil and Cu and Zn concentrations in the plants.

This weak positive correlation indicates that the concentration of the heavy metals in the plants is weakly correlated to the concentration of the heavy metals in the soil. It is thus expected that when the concentration of the heavy metals in

| Species                           | N1 Mean | SE of Mean | N2 Mean | SE of Mean | E1 Mean | SE of Mean | S1 Mean | SE of Mean | W1 Mean | SE of Mean | W2 Mean | SE of Mean |
|-----------------------------------|---------|------------|---------|------------|---------|------------|---------|------------|---------|------------|---------|------------|
| Crinum L.                         | 58.91   | 0.69       |         |            | 50.2    |            |         |            |         |            |         |            |
| Anthephora Schreb.                | 132.92  | 9.31       | 43.17   | 10.31      | 65.78   | 5.92       | 139.63  | 4.03       | 360.7   | 11.62      | 29.35   | 0.49       |
| Digitariaeriantha Stued.          | 135.61  | 8.13       | 144.94  | 3.04       | 64.77   | 2.33       | 1282.2  | 68.71      | 578.9   | 21.71      | 91.4    | 3.05       |
| Sp 21                             | 450.85  |            |         |            | 449     | 1.77       |         |            |         |            |         |            |
| Sp 27                             | 118.86  | 5.22       | 112.47  |            |         |            |         |            | 213.56  | 34.25      |         |            |
| Nephrolepis Schott                | 207.83  | 9.37       |         |            | 221.15  | 22.24      |         |            | 228.15  | 2.59       |         |            |
| Senecio L.                        | 204.78  | 7.44       |         |            | 213.4   |            |         |            |         |            |         |            |
| Arthraxonquartinianus (A. Rich.) Nash | 109.02  | 1016.8     | 454.07  |            |         |            |         |            | 47.53   |            |         |            |
| Amaranthus hybridus L.            | 254.1   | 52.59      | 360.58  | 0.72       | 280.89  | 26.87      | 392.63  |            |         |            |         |            |
| Cyperusrotundus L.                | 20.99   | 46.97      | 1.78    |            |         |            |         |            |         |            |         |            |
| Vernonia Schreb.                  | 167.08  | 51.26      | 588.46  | 13.14      | 434.4   | 184.38     |         |            |         |            |         |            |
| Cymbopogon densiflorus (Steu.) Stapf| 53.78   |            |         |            |         |            |         |            |         |            |         |            |
| Chondrillajuncea L.               | 247.96  | 6.86       |         |            |         |            |         |            |         |            |         |            |
| Crassocephalum Moench.            | 100.88  | 7.38       |         |            |         |            |         |            | 75.92   |            |         |            |
| Conyzacordata Kuntze              | 192.84  | 17.62      |         |            |         |            |         |            |         |            |         |            |
| Kyllinga alba Nees.               | 91.92   | 0.69       |         |            |         |            |         |            |         |            |         |            |
Table 3. Mean concentration of Zn (mg/kg) in the plant species in the sampling sites.

| Species                              | N1 Mean | SE of Mean | N2 Mean | SE of Mean | E1 Mean | SE of Mean | S1 Mean | SE of Mean | W1 Mean | SE of Mean | W2 Mean | SE of Mean |
|--------------------------------------|---------|------------|---------|------------|---------|------------|---------|------------|---------|------------|---------|------------|
| Crinum L.                            | 28.82   | 0.28       |         |            |         |            | 26.47   |            |         |            |         |            |
| Anthephora Schreb.                   | 41.19   | 5.18       | 38.15   | 9.29       | 76.76   | 1.57       | 83.81   | 3.13       | 55.47   | 1.22       | 29.08   | 1.3        |
| Digitariaeriantha Stued.             | 26.16   | 1.19       | 29      | 0.69       | 31.52   | 0.54       | 174.32  | 16.13      | 69.77   | 20.64      | 28.59   | 0.38       |
| Sp 21                                | 64.68   |            |         |            |         |            | 61.82   | 0.77       |         |            |         |            |
| Sp 27                                | 34.64   | 1.42       | 31.06   |            |         |            |         |            | 105.7   | 20.58      |         |            |
| Nephrolepis Schott                   | 53.63   | 4.45       |         |            | 46.14   | 22.15      |         |            | 55.83   | 1.49       |         |            |
| Senecio L.                           | 108.6   | 5.63       | 87.34   |            |         |            |         |            |         |            |         |            |
| Arthraxonquartinianus (A. Rich.) Nash| 72.71   |            | 192.4   | 61.65      |         |            |         |            | 38.84   |            |         |            |
| Amananthus hybridus L.               | 48.24   | 4.7        | 61.26   | 1.08       | 54.98   | 4.55       | 65.22   |            |         |            |         |            |
| Cyperus rotundus L.                  | 27.21   |            |         |            | 38.7    | 0.64       |         |            |         |            |         |            |
| Vernonia                             | 69.95   | 3.66       |         |            | 31.9    | 0.66       | 53.75   | 2.9        |         |            |         |            |
| Cymbopogon densiflorus (Steud.) Stapf|         |            |         |            |         |            |         |            |         |            | 44.9    |            |
| Chondrillajniacea L.                |         |            |         |            |         |            |         |            |         | 59.04      | 2.26    |            |
| Crassocephalum Moench.               |         |            |         |            |         |            |         |            | 57.66   | 1.97       |         | 52.74      |
| Conyzacordata Kuntze                 |         |            |         |            |         |            |         |            |         | 91.51      | 3.43    |            |
| Kyllinga alba Nees.                  |         |            |         |            |         |            |         |            | 33.06   | 0.88       |         |            |

Table 4. Correlation between Cu concentration in the soil and in the plant species.

| Soil Cu Concentration | Concentration of Copper in the plants |
|-----------------------|---------------------------------------|
| Pearson Correlation   | 0.376**                               |
| Sig. (2-tailed)       | 0.000                                 |
| N                     | 175                                   |
| Pearson Correlation   | 1                                     |
| Sig. (2-tailed)       | 0.000                                 |
| N                     | 175                                   |

**Correlation is significant at the 0.01 level (2-tailed).

Table 5. Correlation between concentration of Zn in the soil and in the plant species.

| Soil Zn concentration | Concentration of Zinc in the Plants |
|-----------------------|-------------------------------------|
| Pearson Correlation   | 0.359**                             |
| Sig. (2-tailed)       | 0.000                               |
| N                     | 175                                 |
| Pearson Correlation   | 1                                   |
| Sig. (2-tailed)       | 0.000                               |
| N                     | 175                                 |

**Correlation is significant at the 0.01 level (2-tailed).
the soil is high, the concentration in the plants may be correspondingly high. This was illustrated by the high concentrations recorded in plants that were growing in the study sites having high Cu and Zn concentrations. S1 had the highest Cu and Zn concentrations recorded, 12,024.49 mg/kg and 67.99 mg/kg, respectively. *Digitariaeriantha* had its highest Cu concentration recorded in S1, 1282.2 mg/kg, compared to values of 578.9 mg/kg in W1, 135.61 mg/kg in N1, 144.94 mg/kg in N2, 91.4 mg/kg in W2 and 64.77 mg/kg in E1. *Vernonia* and *Conyzacordata* also had their highest Cu concentrations recorded in S1 (588.46 mg/kg and 192.84 mg/kg, respectively) compared to other quadrants.

This, however, is not always the case, as in some soils, high Cu levels have been shown to be associated with insoluble copper species which have low bioavailability of copper to plants [33]. In addition, plants differ considerably in their ability to assimilate the heavy metals rendering the relationship between soil metal content and metal content in plants unpredictable [34].

### 3.4. Types of Plants Growing at the Study Site

Despite the presence of very toxic concentrations of heavy metals such as Zn and Cu, it is very unlikely to find the tailings dumps or the areas surrounding them devoid of vegetation [35]. This is because there are plants that are able to tolerate the highly toxic concentrations of heavy metals. Most plants collected were annual or perennial herbs and grasses. Some are endemic to Zambia or sub-Saharan Africa, but they are not exclusively endemic to metalliferous areas. Some of the plant species collected have been noted in other parts of the country which do not have metalliferous soils [36]. Since these plants can grow naturally on both metal enriched soils and on no metalliferous soils, they are categorized as pseudometallophytes [37].

A total of 16 plant species were studied, of which, 14 were identified to genus level. Five were from the family Asteraceae, four from family Poaceae, two from Cyperaceae, and one each from Amaryllidaceae, Lomariopsidaceae and Amananthaceae (Appendix 1). In terms of growth habit, nine were herbs, one fern and six grasses.

Of the quadrats studied, N1 was more diverse (species richness = 35%) followed by W2 and N2 (species richness = 18% in both quadrats), while W1 (species richness = 8%) was the least diverse (Figure 2). Species with the highest densities and frequencies were *Anthephora* and *Digitariaeriantha* (density = 39.5 and 40, respectively; frequency = 83.33% each) (Table 6). These two plant species also had a higher abundance (abundance = 47.4 and 48 respectively) and the least abundant was *Crassocephalum* (abundance = 4) and *Chondrillajuncea* (abundance = 3) (Table 6).

Similarity indices showed that N1 and N2 were very similar with respect to species present. S1 and W1 were also quite similar. However, S1 and W2, W1 and W2, were not similar at all. All in all, TD4 and the area 50 m away from it are about 81% similar. The Shannon-Weiner diversity index (H) was found to be
Figure 2. Species richness of the quadrants.

Table 6. Table showing the relative frequency, density and abundance for the species studied.

| Species                         | No. of Individuals | Frequency (%) | Relative Frequency | Density | Relative Density | Abundance | Relative abundance |
|---------------------------------|--------------------|---------------|--------------------|---------|------------------|-----------|-------------------|
| Crinum L.                       | 9                  | 33.33         | 1.1                | 1.5     | 1.1              | 4.5       | 1.5               |
| Anthephora Schreb.              | 237                | 83.33         | 29.08              | 39.5    | 29.08            | 47.4      | 15.83             |
| Digitariaeriantha Stued.        | 240                | 83.33         | 29.45              | 40      | 29.45            | 48        | 16.03             |
| Sp 21                           | 16                 | 50            | 1.96               | 2.67    | 1.97             | 5.33      | 1.78              |
| Sp 27                           | 32                 | 50            | 3.93               | 5.33    | 3.92             | 10.66     | 3.56              |
| Nephrolepis Schott              | 29                 | 50            | 0.25               | 4.83    | 3.56             | 9.67      | 3.23              |
| Senecio L.                      | 16                 | 33.33         | 1.96               | 2.67    | 1.97             | 8         | 2.67              |
| Arthraxonquartinianus (A. Rich.) Nash | 29               | 50            | 0.25               | 4.83    | 3.56             | 9.67      | 3.23              |
| Amaranthus L.                   | 34                 | 50            | 4.17               | 5.67    | 4.17             | 11.33     | 3.78              |
| Cyperus rotundus L.             | 11                 | 33.33         | 1.35               | 1.83    | 1.35             | 5.5       | 1.84              |
| Vernonia Schreb.                | 28                 | 50            | 3.44               | 4.67    | 3.43             | 9.33      | 3.12              |
| Cymbopogon densiflorus (Steud.) Stapf | 15              | 16.67         | 1.84               | 2.5     | 1.84             | 15        | 5.01              |
| Chondrilla funecea L.           | 3                  | 16.67         | 0.37               | 0.5     | 0.37             | 3         | 1                 |
| Crassocephalum Moench.          | 8                  | 33.33         | 0.98               | 1.33    | 0.98             | 4         | 1.34              |
| Conyza cordata Kuntze           | 79                 | 16.67         | 9.69               | 13.17   | 9.7              | 79        | 26.39             |
| Kyllinga alba Nees.             | 29                 | 16.67         | 0.25               | 4.83    | 3.56             | 29        | 9.69              |

2.31 for the control site and 1.84 for TD4. This indicated that there was a richer diversity in the control site compared to TD4.

3.5. Correlation between Shannon-Weiner Diversity Index and Soil Metal Concentration

A negative, but significant correlation was found between the concentration of Cu and Zn in the soil, and the Shannon-Weiner diversity index (Table 7 and Table 8). This means that an increase in Cu and Zn concentration in the soil would result in a decrease in plant species diversity.
Table 7. Correlation between plant species diversity and Cu concentration in the soil.

| Plant Species diversity | Soil_Cu_Concentration |
|-------------------------|------------------------|
| Pearson Correlation     | 1                      |
| Sig. (2-tailed)         | −0.716                 |
| N                       | 6                      |
| Pearson Correlation     | −0.716                 |
| Sig. (2-tailed)         | −0.110                 |
| N                       | 6                      |

Table 8. Correlation between plant species diversity and Zn concentration in the soil.

| Plant Species diversity | Soil_Zn_concentration |
|-------------------------|------------------------|
| Pearson Correlation     | 1                      |
| Sig. (2-tailed)         | −0.648                 |
| N                       | 6                      |
| Pearson Correlation     | −0.648                 |
| Sig. (2-tailed)         | −0.164                 |
| N                       | 6                      |

This highlights the effects of heavy metal pollution in soil on the biodiversity. These findings are corroborated by Vangronsveld et al. (1996) in Chibuike and Obiora [38] who reported that the diversity of higher plant species was very low in areas which were polluted with Zn and Cu. Similarly, Bagatto and Shorthouse [39] noted that an increase in Cu concentration in the soil resulted in a decrease in floral diversity. As such, heavy metal concentration in the soil can predict the species diversity in polluted areas [40]. The effect of heavy metal toxicity, however, varies according to the specific metal involved, but overall impact on the species diversity is negative.

3.6. Categorization of Plants Based on Their Bioaccumulation Factors

Nearly all values of Cu and Zn concentrations recorded in the plants were higher than the recommended values. Nonetheless, plants have developed mechanisms that allow them to thrive in toxic environments. And it is these plants that have a high probability of being potential phytoremediators. Excluders only tolerate metals in the substrate by restricting the uptake of metals into the roots [15]. Accumulators on the other hand present specialized mechanisms that allow them to accumulate or even hyperaccumulate metals in their shoots [12].

Hyperaccumulation of Zn is exceptionally rare due to the readiness with which it can be precipitated as the insoluble sulfate in the rhizosphere, thus minimizing the probable uptake and transport to the shoots of the plants [36]. In various research conducted so far, 13 taxa have been identified as Zn hyperac-
cumulators [36]. The bioaccumulation factors calculated showed that *Crinum* (BAF = 0.86) is a Zn excluder, *Arthraxonquartinianus* (BAF = 10.77) is a Zn hyperaccumulator and the remaining 14 species (BAF ranging from 1.07 - 4.12) are all Zn accumulators (Table 9).

A number of Cu hyperaccumulators have been identified all over the world which include *Beciumcentralafricanum, Bulbostyliscupricola, Pimpinella acutidentata, Cheilanthesperlanata, Eragrostisracemosa, Bulbostylispseudoperennis, Aspilia ciliate* and *Glycine wightii* var. *Longicaud, Conyzacordata, Persicariapuncata and Persicariacapitata* [22] [23] [41] [42]. However, in this study, no Cu hyperaccumulator was identified. All the plant species were found to be Cu excluders (BAF ranging from 0.01 to 0.77) (Table 10).

It is possible that part of the measured Cu and Zn in the plant samples may have been from external deposition not removed completely during sample washing. Faucon *et al.* in Ghaderian and Ravandi [36] highlighted the fact that improperly washed specimen tended to have relatively high concentration values of heavy metals, hence the need to carry out further research on plant species identified tentatively as hyperaccumulators.

The high number of Zn and Cu excluders found in this study attests to findings of other researchers that the majority of metal tolerant plants colonizing mineral wastes are excluders [36] [42].

**Table 9.** Categorization of plant species based on their BAF Cu values.

| Species                                      | BAF (TD4) | BAF (Immediate Vicinity) |
|----------------------------------------------|-----------|--------------------------|
| *Crinum* L.                                  |           | 0.01                     |
| *Antheaphora Schreb.*                        | 0.04      | 0.02                     |
| *Digitariaeriantha Steud.*                   | 0.1       | 0.04                     |
| *Sp 21*                                      | 0.77      | -                        |
| *Sp 27*                                      | 0.04      | 0.35                     |
| *Nephrolepis Schott.*                        | 0.03      | 0.05                     |
| *Senecio L.*                                  |           | 0.24                     |
| *Arthraxonquartinianus (A. Rich.) Nash.*     | -         | 0.5                      |
| *Amaranthus hybridus* L.*                    |           | 0.07                     |
| *Cyperusrotundus* L.*                        | 0.01      | 0.02                     |
| *Vernonia Schreb.*                            | 0.1       | 0.15                     |
| *Cymbopogon densiflorus* (Steud.) Stapf.*    | -         | 0.01                     |
| *Chondrillaajunccea* L.*                     |           | 0.35                     |
| *Crassocephalum Moench.*                     | -         | 0.01                     |
| *Conyzacordata Kuntze.*                      | 0.03      | -                        |
| *Kyllinga alba Nees.*                        | 0.09      | -                        |
Table 10. Categorization of plants based on their BAF Zn values.

| Species                          | BAF (TD4) | BAF (Immediate vicinity) |
|----------------------------------|-----------|--------------------------|
| Excluders                        |           |                          |
| Crinum L.                        | -         | 0.86                     |
| Antheephora Schreb.              | 1.73      | 1.26                     |
| Digitariaeriantha Steud.         | 1.89      | 1.07                     |
| Sp 21                            | 2.3       | -                        |
| Sp 27                            | 1.28      | 3.92                     |
| Nephrolepis Schott.              | 1.68      | 1.93                     |
| Senecio L.                       | -         | 4.12                     |
| Amaranthus hybridus L.           | -         | 2.05                     |
| Cypersusrotundus L.              | 1.22      | 1.31                     |
| Vernonia Schreb.                 | 1.91      | 3.18                     |
| Cymbopogon densiflorus (Steud.) Stapf. | -     | 1.66                     |
| Chondrillajuncea L.              | -         | 1.95                     |
| Crassocephalum Moench.           | -         | 1.95                     |
| Conyzacordata Kuntze.            | 1.56      | -                        |
| Kyllinga alba Nees.              | 1.26      | -                        |
| Hyperaccumulator                 | Arthraxonquartinianus (A. Rich.) Nash | 10.77 |

4. Conclusions

With respect to Zinc, Crinum was found to be an excluder, Arthraxonquartinianus a hyperaccumulator, while the remaining plant species were accumulators. All the 16 plant species were found to be Cu excluders. The plant species identified in this study, thus, have potential for phytoremediation as excluders, accumulators and hyperaccumulators. They represent potential for remediation of soils heavily polluted by heavy metals.

Further research needs to be done to identify indigenous plants with potential for phytoremediation of other heavy metals such as Cobalt, Nickel, Lead and Cadmium.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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### Appendix 1

**Table A1.** List of plant species studied.

| Plant species       | Family             | Habit | Life Cycle |
|---------------------|--------------------|-------|------------|
| *Crinum L.*         | Amaryllidaceae     | Herb  | Perennial  |
| Anthephora Schreb.   | Poaceae            | Grass | Perennial  |
| Digitariaeriantha Stued. | Poaceae         | Grass | Perennial  |
| Sp 21               | n.a.               | Herb  | n.a.       |
| Sp 27               | n.a.               | Herb  | n.a.       |
| Nephrolepis Schott  | Lomariopsidaceae   | Fern  | Perennial  |
| Senecio L.          | Asteraceae         | Herb  | Perennial  |
| Arthraxonquartinianus (A. Rich.) Nash | Poaceae | Grass | Perennial  |
| Amaranthus hybridus L. | Amaranthaceae    | Herb  | Annual     |
| Cyperus rotundus L.  | Cyperaceae         | Grass | Perennial  |
| Vernonia Schreb.     | Asteraceae         | Herb  | Perennial  |
| Cymbopogon densiflorus (Steud.) Stapf | Poaceae | Grass | Perennial  |
| Chondrillajuncea L.  | Asteraceae         | Herb  | Perennial  |
| Crassocephalum Moench. | Asteraceae     | Herb  | Annual     |
| Conyzacordata Kuntze | Asteraceae         | Herb  | Perennial  |
| Kyllinga alba        | Cyperaceae         | Grass | Perennial  |