



Native plant species screening for phytogeochemical exploration in the Zambian Copperbelt

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ABSTRACT

Trace element analysis of plant tissues can aid mineral exploration for sediment hosted Cu-Co deposits in the Zambian Copperbelt (ZCB). This study was conducted at the Mitumba prospect, an area in the ZCB known to have copper minerals but no historical mining activities, to identify native plant species and their tissues that are most indicative of mineralized zones. Field inventory and ecological analysis identified 22 native plant species from 12 different families, of which Fabaceae (36.4%) was dominant. At species level and based on the coating index, we identified several predominant species, among them, *Haumaniastrum katangense* (Lamiaceae), *Aframomum angustifolium* (Zingiberaceae), *Brachystegia boehmii* (Fabaceae), and *Diplorynchus condilocarpon* (Apocynaceae). Sampling was undertaken of soils and plant organs above the known mineralized zone and at control points outside of the mineralized area. Most species translocated Cu from the roots to the aboveground biomass as indicated by translocation factors (TF) > 1 but only three species, namely, *Haumaniastrum katangense*, *Aframomum angustifolium* and *Diplorynchus condilocarpon* can both translocate and bioconcentrate (BCF > 1) bioavailable Cu from the rhizosphere, making them ideal candidates for phytogeochemical exploration. Only *Haumaniastrum katangense* and *Aframomum angustifolium* accumulated Co. Plant roots and leaves demonstrate significant Cu anomalism and show a wider population of anomalous values compared to the soils. Statistical and machine learning techniques both indicate significant relationships between soil Cu concentration and the content of Cu in plant roots and leaves highlighting soil pH, organic matter and clay content as the major physicochemical variables influencing metal bioavailability in soil-plant systems.

1. Introduction

The floristic composition of the Central African Copperbelt (CACB) which extends between northern Zambia and southern DRC is characterized by several taxa that have adapted to elevated soil Cu and/or Co concentrations. Such plants are classified as excluder, indicator, and hyperaccumulator species depending on their response mechanisms to the geochemical environment (w. Ilunga et al., 2015; Pollard et al., 2014). Excluders localize trace elements in their roots and generally maintain low leaf concentrations over a wide spectrum of soil metal concentrations. In contrast, indicator and hyperaccumulator species can absorb, accumulate and translocate trace elements from the soil to the aboveground plant organs (Anand et al., 2007); hyperaccumulator plants

show excess metal uptake and translocation into their leaves (Pollard et al., 2014; Verbruggen et al., 2009). Several geobotanical studies describing such metal tolerant plants were conducted in the CACB during the 1950–60s (Tooms and Webb, 1961), a period marking the discovery of many of the district's ore deposits. In the Zambian Copperbelt (ZCB), all the known ore bodies except for the Chambishi southeast ore body cropped out at the Earth's surface. Discovery of deposits was primarily accomplished by prospecting and geological mapping (Mukube et al., 2024; Tooms and Webb, 1961). This early prospecting work employed identification of native plants such as *Becium homblei*, *Haumaniastrum katangense*, and *H. robertii* as indicators of ore deposits (Morrison

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et al., 1979) although their Cu-Co accumulation patterns relative to the underlying mineralized rocks were unclear at the time.

Currently, mineral exploration in the Copperbelt region targets areas covered by residual and transported overburden to locate shallowly to deeply buried ore bodies. Exploration is hindered by dense vegetation and thick regolith profiles. In the past decades, surficial geochemical data of different types including soils, stream sediments, and groundwater have been used for both mineral exploration and environmental assessments (Fontaine et al., 2020; Křibek et al., 2010; Master and Ndhlovu, 2019). Phytogeochemistry potentially offers promising advantages (Cui et al., 2021) to identify geochemical footprints of buried mineralized areas blind to other surficial media and could be particularly potentially useful in the deeply weathered ZCB. This is because plant roots can penetrate thick overburden material and subsequently translocate geochemical signatures from the roots to above-ground plant organs (Henne et al., 2021; Krasavtseva et al., 2023; Rasti et al., 2020). Phytogeochemical anomalies may also have the potential to display relatively wide dispersion halos due to the extensive reach of plant root systems (Dunn and Christie, 2019; Ghorbani et al., 2022; Johnsen et al., 2021). Phytogeochemistry has gained considerable attention in different parts of the northern hemisphere and in some tropical regions (Anand et al., 2007; Ghorbani et al., 2022; Johnsen et al., 2021; Lottermoser et al., 2008; Nkoane et al., 2005). For instance, Cole et al. (1978) located Cu mineralized zones affected by shallow weathering using *Helichrysum leptolepis* in the Ghanzi area of Botswana. In the same study, the species *Ecbolium lugardiae* was used to indicate Cu ore bodies concealed by thick Kalahari sand cover in the Ngwako Pan area. A pilot study conducted using both phytogeochemical and conventional soil sampling on areas of transported overburden in Australia indicated that *Acacia aneura* showed strong multi-element anomalism over a buried mineralized area as compared to soil geochemistry which demonstrated weak and ambiguous Pb-Zn mineralization signatures (Anand et al., 2007). Phytogeochemical studies across the CACB have most recently focused on restoration of mining generated wastelands (w. Ilunga et al., 2015; Lange et al., 2018; Matakala et al., 2023). These studies demonstrate Cu-Co hyperaccumulation with certain species being absolute metallophytes that are exclusive to mineralized areas (Boisson et al., 2016; Leteinturier et al., 2001). For instance, the species, *H. robertii* grows only over copper deposits in both Zambia and DRC with geochemical values in its leaves reaching 8500 ppm Cu and 4000 ppm Co (Faucon et al., 2012).

To effectively evaluate the utility of phytogeochemistry requires research to not only identify target species but also define the most useful plant organs for phytogeochemical sampling. This study aims to identify autochthonous plant species growing over the Mitumba Cu-Co prospect and assesses the feasibility of employing targeted species as indicators for buried mineral deposits. In addition, the study seeks to develop predictive models for Cu and/or Co uptake in soil-plant systems of the Mitumba prospect using a range of soil variables. We determined Cu and Co concentration in the B-horizon soil samples and in the different tissues (roots, stems, and leaves) of twenty-two plant species. This allowed determination of element translocation and bioconcentration factors (BCF) of metals in the plants. Statistical and machine learning (ML) techniques were then employed to select the species most indicative of mineralized zones and the relevant soil properties that influence Cu and Co uptake in these plant species.

2. Materials and methods

2.1. Study area

The Mitumba Cu-Co prospect (13° 30'E – 13° 33'E, 27°24'N – 27°31'N) lies to the west of the ZCB and covers an areal extent of 60 km² (Fig. 1). While the stratigraphic position for most mineralized rocks in the ZCB including the Mitumba Cu-Co prospect is the Lower Roan Group at the base of the Katanga Supergroup sequence (Fig. 1),

ore deposits and prospects are known from the basement upwards into the Nguba Group. Mineralized zones containing the copper minerals malachite, chrysocolla, and chalcocite in bedrock beneath surficial regolith were identified in the Mitumba Cu-Co prospect by aircore drilling over a strike length exceeding 1 km and a width of 300 m. The area has never been mined. Alteration associated with deposits in the Copperbelt ranges from early magnesian (anhydrite, dolomite, magnesite, Mg-chlorite, and tourmaline) to potassic (K-feldspar to local sericite), and sometimes late-stage sodic alteration (Bull et al., 2011; Hitzman David and Stuart, 2010). Unpublished reports of the lithogeochemical analysis of rock chip samples from the Mitumba prospect shows a geochemical association of Cu-As-Ni-V-Mo-Bi ± Zn. This reflects the geochemical signature of most deposits in the ZCB (Ettler et al., 2011; Giger and Kinnaird, 2017).

The majority of ore deposits in the ZCB are associated with regional geological structures, particularly syndimentary normal faults or anticlinal structures related to basin inversion (Koegelenberg et al., 2019). Such structures probably served as pathways for mineralizing fluids and may later have enhanced groundwater flow enabling metal availability in both groundwater and soils for potential uptake by plant species. Soils in the study area are predominantly residual with a reddish-brown color and a pH ranging from 4.7 to 8.6. These soils support a vegetation cover mainly consisting of Miombo woodland which has a diversity of plant species. The Miombo ecosystem has several species which have demonstrated ability for absorption and accumulation of Cu and associated metals (Chileshe et al., 2020; Festin et al., 2019a) and *H. katangese*, *A. angustifolium*, and *E. africanum* which have shown useful applications in ecological restoration studies of mining degraded landscapes (Carrick and Krüger, 2007; Festin et al., 2019a). In addition, *Marquesia macroura* which has a deep-rooting system is generally widespread in the study area.

2.2. Sample collection and analysis

Phytogeochemical sampling was conducted along NW-SE transects over the Mitumba prospect. The sampling was done perpendicular to the known strike of the subcropping mineralized zones (Fig. 1). A quantity of approximately 300 g of all specimens sampled was collected from each sampling station. Quadrat quantitative techniques (Rahman et al., 2020) were applied in which root, stem, and folia samples were collected for different quadrat sizes including 100 m², 25 m², and 1 m² for trees, shrubs, and herbs respectively. Plant species identification in the field was aided by botanists from the Zambia Forest Research Centre. Soil samples were also collected at each sampling site. In total, 1170 samples of roots, stems and leaves and 1170 samples of soil were collected and analyzed: three plant species and three soil samples were collected per plot for three plots at 130 sampling sites. The selection of samples in plant-soil systems of the Mitumba Cu-Co prospect was performed with respect to density, frequency, and surface area of the sampling site. Plant species importance and predominance was numerically categorized from 1–4 (Table 1) using a coating index (Matanzas et al., 2021).

Overall, twenty-two species were collected from the study area including prospective and non-prospective zones within an area of approximately 15 Km². In addition, 61 control samples of the corresponding plant species were randomly collected from an area devoid of anthropogenic activities and distal to the Mitumba soil Cu anomalous zone, i.e., about 3.5 km to the west of the Cu anomaly (Fig. 1). Sample collection was performed, wearing untreated leather gloves and the samples were cut using garden clippers. All soil samples were collected from the B-horizon (30–60 cm) using a hand auger because this is a soil horizon with a chemical composition that often reflects bedrock geochemistry and associated alteration (Reimann, 1988). Both plant and soil samples were placed in well aerated and labeled clean polythene plastic bags during the sampling campaign. The samples were transported to the Copperbelt University laboratory where they

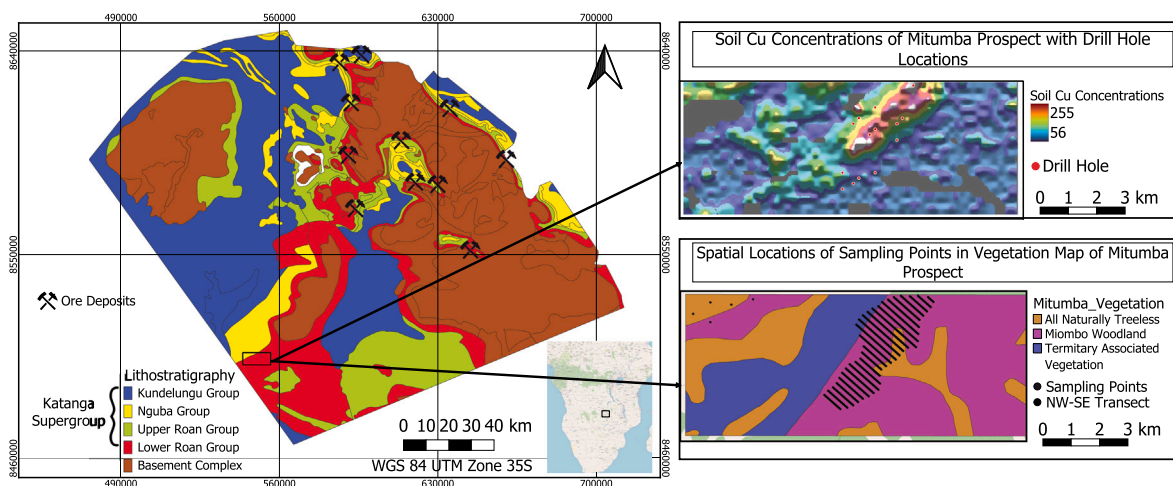


Fig. 1. Geological map of the ZCB with the Mitumba copper prospect soil Cu concentration in ppm and vegetation cover. The geological map was redrawn from data obtained from the Geological Survey of Zambia. The geochemical Cu map was interpolated from data collected by the license holder of the Mitumba prospect. The vegetation map was redrawn from data obtained from the Zambia Forest Research Centre.

Table 1
Coating Index Categories employed during plant species sampling.

Coating index class	Explanation
1	Moderately abundant species but poor area coverage from 1%–10% (median coating = 5%)
2	Abundant species covering between 10%–25% of the surface (median coating = 17.5%)
3	Varying number of species covering between 25%–50% of the surface (median coating = 37.5%)
4	Varying number of species covering between 50%–75% of the surface (median coating = 62.5%)

were prepared prior to analysis. In the laboratory, soil samples were air dried for 72 h and then pulverized and sieved to 180 mesh to obtain an ideal size fraction of each sample that was repackaged in a well labeled sample plastic bag. Similarly, the respective plant organs of each species from each sample site were washed with deionized water prior to air drying for 72 h. This was especially important for plant roots to ensure all soil particles were removed. Mortar and pestle were used to homogenize the plant organs of each of the species that were collected to ensure uniform size fractions.

Physicochemical characterization of the soil samples was conducted using standard procedures of 3 determinations per sample. The soil clay content was estimated using an approach based on Wäldchen et al. (2012). pH and electrical conductivity measurements were taken from a 1:2.5 suspension of soil and distilled water using a glass electrode pH meter and conductivity meter respectively (Lu et al., 2023). Soil organic matter was measured using the loss-on-ignition approach (Schulte and Hopkins, 1996) based on weight loss at a temperature of 450 °C.

Chemical analysis was performed on both plant and soil samples by means of a Niton xl3t GOLDD+ portable X-ray fluorescence (pXRF) analyzer. The ability of pXRF analyzers to accurately detect and quantify Cu and Co in plants and biological materials has been demonstrated by several studies (Bull et al., 2017; Monot et al., 2024; Turner et al., 2018; van der Ent et al., 2019). In addition, the Niton xl3t GOLDD+ pXRF can detect low concentrations of trace elements in plant species when set in AllGeo and soil modes (Monot et al., 2024). Quality assurance and quality control (QA/QC) procedures confirming the reliability of the elemental analysis were performed by analyzing a certified reference material, OREAS 45b. This reference material had Cu and Co contents of 449 ± 0.05 ppm and 73.8 ± 0.05 ppm respectively. The measured

results for these elements averaged 435 ppm and 76 ppm. In addition, one in every 10 samples was selected for triplicate experiments to reduce errors, and the relative standard deviation of the samples was ±5% of the mean. In addition, we utilized the collected control samples to check the precision and accuracy of the analytical results. The quality check for the control samples was performed using the formula $\Delta \lg C_j - \Delta \lg C_s \leq \pm 0.13$, where C_j and C_s are the mean of n measurements and the value of the standard sample respectively. In this case, repeated analysis of the same sample should meet the standard of relative deviation (RD) ≤ 20%. The QA/QC results indicate that control samples passed the pre-test criteria with the relative deviation of repeated experiments of the same sample ranging from 0.1%–3.7%. This conforms to the standard of RD ≤ 20%, indicating the integrity and reliability of the analytical test results. As such, we analyzed soil and ash from plant roots, stems, and leaves of each species separately by setting the pXRF in soil mode and an analysis time of 60 s.

2.3. Translocation, bioconcentration and accumulation factors

Cu and Co concentrations in soils and respective plant species were used to determine the biological concentration factor (BCF) and Translocation factors (TF). The BCF forms the basis upon which the concentration, transfer, and accumulation of metals from the soil and underlying mineralized rocks to the plant is evaluated. The BCF was determined from the ratio of the plant root metal concentration to that in soil (Yoon et al., 2006). To model the plant's ability to sequester and concentrate metals from the soil to the roots, the BCF was calculated as:

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

Where C_{plant} is the metal concentration in the respective plant root (mg kg^{-1}), and C_{soil} represents the soil metal concentration (mg kg^{-1}) for a given sample plot.

Metal translocation factors within the plants were calculated from the ratio of the leaf metal concentration to that of the roots (Yanqun et al., 2005). As such, we determined the TF of each of the sampled species using the formulae:

$$TF = \frac{C_{\text{leaf}}}{C_{\text{root}}} \quad (2)$$

where C_{leaf} and C_{root} are the metal concentrations in the respective leaves and roots of each of the sampled plant species. A BCF and TF greater than one (BCF and TF > 1) indicates the potential for

phytogeochemical application of a given plant species (Ouyang et al., 2024). In addition, the suitability of plant species for indicating buried mineral deposits was evaluated using the accumulation factor (AF) which measures the ratio of metal concentration in plant leaves to that in the soil:

$$AF = \frac{C_{\text{leaf}}}{C_{\text{soil}}} \quad (3)$$

. These phytogeochemical indices, BCF, TF, and AF form the basis for the selection of accumulator and hyperaccumulator species that are relevant to mineral exploration targeting.

2.4. Statistical analysis

Robust statistical analysis was employed in phytogeochemical data processing to determine which of the plant tissues may be useful sampling media in mineral exploration. Univariate statistical approaches including descriptive statistics and exploratory data analysis were employed to identify patterns, trends, and structure in the phytogeochemical data. The descriptive statistics were in the form of tables recording the statistical counts, mean, and standard deviation of elements in each of the plant organs of the sampled species. For censored values in the phytogeochemical data (i.e., data below limit of detection, <LOD), we employed a method proposed by Hron et al. (2010) that is based on the use of nearest neighbors to estimate replacement values. In addition, the phytogeochemical data was log transformed to address the closure problem which is a common feature of geochemical datasets (Grunsky and de Caritat, 2020). This approach was implemented in the R package, “robCompositions” in R studio. The relationships between the different organs of sampled plant species and the subsoil were constrained by Spearman correlation analysis. Correlation analysis was conducted to estimate the strength of statistical relationships between plant tissues and the soil cover over the mineralized Mitumba Cu-Co prospect. High coefficient of correlation value (i.e., -1 or 1) shows a good relationship between two variables at a significant level of $P < 0.05$. Variables with correlation coefficients, $r > 0.7$ are considered as strongly correlated while r between 0.4 and 0.7 are moderately correlated. Prior to the application of correlation analysis, we standardized the phytogeochemical data as suggested by Zuo et al. (2013).

An assessment of the nature of the distribution of Cu and Co values including the presence of outliers in both soil and plant tissues was done through exploratory data analysis (EDA). The distribution patterns of Cu and Co in soil and plant tissues was performed using probability plots and box and whisker plots. Probability plots have long been recognized as useful exploratory data analysis criteria for geochemical anomaly detection (Esmailoghli and Tabatabaei, 2020; Filzmoser et al., 2005; Stanley and Sinclair, 1987). Threshold values in both soil and plant tissues were determined by identifying data values indicating a change in the slope along the probability plot. These methods enabled the recognition and detection of anomalous values in the plant tissues since discrimination of anomalous values from background values is the first and most important step in mineral exploration (Yusta et al., 1998). Anomalies indicate both enrichment and depletion of certain elements that may provide a geochemical footprint of the subcropping ore bodies. In this study, we focused on the identification of positive and significant Cu and Co anomalies or enrichment values in plant tissues that may be related to mineralized zones in the Mitumba prospect. When box and whisker plots are used to indicate enrichment values in mineral exploration campaigns, estimation of the inner and outer fences becomes crucial (Yusta et al., 1998). Based on this method, outliers are data values beyond the inner and outer fences. The fences were estimated based on the formulae suggested by Reimann and Garrett (2005):

$$\text{Inner fences: } f_l = Q1 - k \times IQR; f_u = Q3 + k \times IQR, \text{ where } k = 1.5 \quad (4)$$

$$\text{Outer fences: } f_l = Q1 - k \times IQR; f_u = Q3 + k \times IQR, \text{ where } k = 3 \quad (5)$$

In Eqs. (4) and (5) above, Q1 and Q3 represent the first and third quartiles or the 25th and 75th percentiles of the phytogeochemical data, respectively. The difference between Q3 and Q1 is the interquartile range (IQR). Data values lying between inner and outer fences are mild outliers whereas those that lie beyond the outer fences are far outliers or geochemical anomalies.

2.4.1. Testing the significance of the anomalies (MWW test)

The significance of anomalism in the plant tissues was conducted by comparative statistical analysis of samples collected over both mineralized and non mineralized sampling sites. To determine whether the element concentrations above mineralized areas differ from the background values in a statistical sense, we divided the sampling points into two categories based on the known lithological units of the Mitumba drill core logging. We collected samples directly over drill spoils that intercepted mineralized rocks with Cu ores at depths (20–50 m and 75–100 m) while background samples included all the samples distal to mineralized zones. We used the non-parametric Mann–Whitney–Wilcoxon test (Sultan et al., 2020) to compare the distributions of the on-deposit and background samples. In this regard, we set the null hypothesis stating that: “The distribution of the two sets of samples under consideration i.e., on- mineralized zones and in the background, represent the same distribution”. This test was implemented in Python code by importing mannwhitneyu from SciPy. Stats.

2.5. Element uptake models in soil-plant systems

Element uptake in soil-plant systems is commonly modeled using the Freundlich-type function (Cipullo et al., 2019; Ding et al., 2014; Rodríguez et al., 2008) that is denoted as:

$$\log C_{\text{plant}} = a + b \log C_{\text{soil}} \quad (6)$$

Where C_{plant} and C_{soil} are plant and soil metal concentrations as earlier indicated in equation one. In this study, stepwise multiple linear regression (SMLR) with selected independent soil variables were employed to obtain extended Freundlich-type functions for prediction of Cu and Co uptake in soil-plant systems. The architecture of the regression model excluded soil variables that were below the minimum level of statistical significance ($p > 0.05$). Average Cu and Co concentrations of respective plant organs coupled with soil physicochemical properties from the Mitumba Cu-Co prospect, including pH, electrical conductivity, clay content, and organic matter were used to develop SMLR models. The most important soil properties that significantly influence metal bioavailability and uptake in plants were selected based on correlation analysis. Thus, predictive models for Cu and Co uptake in respective plant organs were developed by adding soil variables in a step-by-step fashion to determine the soil properties required for an optimal model. The models were evaluated based on the explanatory power (R^2) and the predictive accuracy.

To analyze the spatial variation of Cu and Co uptake in the respective plant organs with respect to soil properties, the self-organizing maps (SOM) algorithm was employed. SOM is a type of unsupervised artificial neural network (ANN) that can perform a non-linear projection of a high dimensional data space onto a two-dimensional array of neurons (Kohonen et al., 1996). The ability of SOM to intuitively detect nonlinear relationships makes it preferable to other methods such as principal component analysis (PCA) and factor analysis which assume linear relationships among input variables (Dollhopf et al., 2001). In this study, a two-layer SOM model comprising an input layer with the same number of neurons as the input variables and an output layer produced from neurons organized on a two-dimensional grid was generated. Every input neuron was assigned to an output neuron. The number of neurons was primarily determined using a widely accepted approach in which the number of neurons (n) = (number of samples)^(-1/2) (Vesanto, 2000), and the analysis of topographic and quantization errors enabled the modification of the final map

Table 2

Autochthonous plant species observed in Mitumba Cu-Co prospect with consideration of Coating index (abundance, coverage, density, and frequency). GH: Growth habit.

Botanical family	Scientific name	GH	Coating index
Lamiaceae	<i>Haumaniastrum katangense</i>	Herb	4
Zingiberaceae	<i>Afromomum angustifolium</i>	Herb	4
Fabaceae	<i>Brachystegia boehmii</i>	Tree	4
Fabaceae	<i>Afzelia quanzensis</i>	Tree	3
Fabaceae	<i>Brachystegia floribunda</i>	Tree	3
Apocynaceae	<i>Diploryhncus condilocarpon</i>	Tree	3
Dipterocarpaceae	<i>Marquesia macroura</i>	Tree	3
Orchidaceae	<i>Eulophia mumbwaensis</i>	Herb	3
Passifloraceae	<i>Paropsia brazeana</i>	Shrub	3
Fabaceae	<i>Eriosema shireense</i>	Herb	3
Verbenaceae	<i>Vitex doniana</i>	Tree	3
Fabaceae	<i>Isobertlinia angolensis</i>	Tree	2
Fabaceae	<i>Albizia adianthifolia</i>	Tree	2
Fabaceae	<i>Baphia baquaertii</i>	Tree	2
Dipterocarpaceae	<i>Monotes africanus</i>	Tree	2
Dioscoreaceae	<i>Dioscorea aristeriscus</i>	Shrub	1
Sapotaceae	<i>Chrysophyllum bangweolense</i>	Tree	1
Umbelliferae	<i>Steganotaenia araliacea</i>	Tree	1
Fabaceae	<i>Erythrophleum africanum</i>	Shrub	1
Myrtaceae	<i>Syzygium guineense</i>	Tree	1
Cyperaceae	<i>Bulbostylis capillaris</i>	Herb	1
Verbenaceae	<i>Vitex mombassae</i>	Tree	1

dimension ratios. Competitive learning was used as a training approach, and this occurred over several iterations leading to a cluster of winning neurons that correlate with clusters of input data (Kohonen, 1998). The SOM process was performed using the ioGAS-64 software (Raatikainen et al., 2025), an advanced geoscience analytics system for exploration and environmental analysis.

3. Results

3.1. Floristic composition

The Mitumba Cu-Co prospect revealed the presence of twenty-two plant species that have been grouped into 12 families. Three species namely, *H. katangense*, *A. angustifolium*, and *B. boehmii* were identified as the most dominant in the study area based on the highest coating index (Table 2). The study habitat indicated the presence of both tree and herbaceous species of different families. Most of the observed species belong to the Fabaceae botanical family which accounted for 36.4% of the study habitat.

Based on the quadrat sampling technique and subsequent calculation of the coating index (CoI), the most important and predominant plants in the study area are herbaceous species particularly, *H. katangense* and *A. angustifolium* of the Lamiaceae and Zingiberaceae families. These herbaceous species occur along with the tree specie, *B. boehmii* of the Fabaceae family. In addition, isolated tree and shrubby species of minimum CoI were observed within the Mitumba Cu-Co prospect. These species include *D. aristeriscus*, *C. bangweolense*, *S. araliacea*, *E. africanum*, and *S. guineense*.

3.2. Soil physicochemical characterization

The major edaphic parameters of the soil samples that were collected over areas of maximum CoI in the Mitumba Cu-Co prospect are shown in Table 3. The results indicated a generally homogeneous soil profile across the sites of high CoI; the soils showed no salinity with moderately acidic pH values, and the organic matter and clay contents were low.

Table 3

Physicochemical characterization of soil samples (n = 1,170) from the Mitumba Cu-Co prospect.

Soil parameter	Units	Mean	Std. Deviation
pH	1:2.5 H ₂ O	6.2	0.79
C.E ¹	dS m ⁻¹	0.014	0.003
O.M ²	%	2.76	0.31
Clay content	g kg ⁻¹	15.4	3.84

3.3. Copper and cobalt concentration in soil – plant systems

The average Cu and Co concentration in soil and plant organs from the study area are shown in Table 4. The soil Cu concentration varied between 77–248 mg kg⁻¹ while Co concentration was in the range of 80–270 mg kg⁻¹. Elevated soil Cu and Co concentrations were found in zones characterized by a CoI of 3–4 across the sampling sites of the study area and this also correlated with the previously defined soil geochemical anomaly by the tenement holder of the Mitumba Cu-Co prospect. High values of Cu and Co were associated with acidic soils and comparatively low contents of organic matter. Average concentrations of Cu and Co in the tissues (roots, stems, and leaves) of different plants from the Mitumba Cu-Co prospect are shown in Table 4. The results indicated that stems had the lowest average Cu concentration with some species not showing any presence of Cu and Co. Leaves showed high values of Cu except for the species, *B. floribunda* and *P. brazeana* that had higher root Cu concentration. Plant leaves had Cu concentrations ranging from 100–426 mg kg⁻¹. Co was only detected in two of the sampled species notably, *H. katangense* and *A. angustifolium* which showed elevated root Co concentration and a BCF > 1 even though the translocation and accumulation factors were very low.

Correlation analysis showed varying relationships between soil and plant tissue Cu concentrations (Fig. 2). A strong and significant statistical correlation ($r = 0.94$, $p < 0.05$) between soil and root Cu concentration was observed in the 22 species. Leaf Cu concentrations in the 22 species showed moderately significant correlation ($r = 0.47$, $p < 0.05$) with the soil Cu content. The correlation between stem Cu concentration and soil Cu content was very weak but statistically significant ($r = 0.10$, $p < 0.05$). There is a notable difference between the Cu accumulation patterns in the plant tissues and observed correlation with the soils overlying the mineralized rocks of the Mitumba Cu-Co prospect. The relative Cu absorption pattern which was in the decreasing order of leaves > roots > stems differ from the statistical relationships between plant tissues and soil Cu content in which roots had the highest correlation coefficient.

3.4. Translocation and bioconcentration factors

The ability to translocate Cu and Co from the roots to the above-ground biomass was evaluated by calculation of TF (Table 4). Metal translocation from the roots to the aerial parts of the plant is only known to occur when the TF values are greater than 1 (Krasavtseva et al., 2023). Ten species from six different families had TF values > 1. The highest TF value (1.77) was indicated by the herbaceous plant, *E. shireense* of the Fabaceae family. Tree species that were observed to significantly translocate Cu from the roots to aboveground biomass in the study area are *M. Macroura* and *A. adianthifolia* which have TF values of 1.63 and 1.51 respectively. While most species in the study area can effectively translocate Cu from the roots to the aboveground plant organs, only three species were able to sequester significant quantities of bioavailable Cu from the rhizosphere (a dynamic soil environment where complex interactions between roots, minerals, organic compounds, solutes, gases and micro-organisms occur). The three species namely, *A. angustifolium*, *H. katangense*, and *D. condilocarpon* had a BCF > 1 (Fig. 3). Cu bioconcentration in the study area was

Table 4
Mean Cu and Co in soils and plant tissues reported in the Mitumba Cu-Co prospect. Bioconcentration factors (BCF), translocation factors (TF), and accumulation factors (AF) are shown.

Specie	Element	Concentration (mg kg ⁻¹)				BCF	TF	AF
		Soil	Root	Stem	Leaf			
<i>Haumaniastrum katangense</i>	Cu	87	146.3		161.4	1.68	1.10	1.86
	Co	156	467		125.7	2.99	0.27	0.81
<i>Afromomum angustifolium</i>	Cu	65.8	137.7		142	2.09	1.03	2.16
	Co	197.4	228		55	1.16	0.24	0.28
<i>Brachystegia boehmii</i>	Cu	216	127	47	139.7	0.59	1.10	0.65
<i>Afzelia quanzensis</i>	Cu	195	143		152	0.73	1.06	0.78
<i>Brachystegia floribunda</i>	Cu	247	183	75	133.4	0.74	0.73	0.54
<i>Diploryhncus condilocarpon</i>	Cu	95	134	120	148	1.41	1.10	1.56
<i>Marquesia macroura</i>	Cu	209	105	53	171	0.50	1.63	0.82
<i>Eulophia mumbwaensis</i>	Cu	287	102		149.3	0.36	1.46	0.52
<i>Paropsia brazeana</i>	Cu	179	167		150	0.93	0.90	0.84
<i>Eriosema shireense</i>	Cu	180	87		154	0.48	1.77	0.86
<i>Vitex doniana</i>	Cu	167	147	59	156	0.88	1.06	0.93
<i>Isobertlinia angolensis</i>	Cu	245		84	149.7	–	–	0.61
<i>Albizia adianthifolia</i>	Cu	175	98	67	148.2	0.56	1.51	0.85
<i>Baphia baquaertii</i>	Cu	146	131		125	0.90	0.95	0.86
<i>Monotes africanus</i>	Cu	167		61	127	–	–	0.76
<i>Dioscorea aristeriscus</i>	Cu	304			156	–	–	0.51
<i>Chrysophyllum bangweolense</i>	Cu	234		56	109	–	–	0.47
<i>Steganotaenia araliacea</i>	Cu	255			161	–	–	0.63
<i>Erythrophleum africanum</i>	Cu	199			150	–	–	0.75
<i>Syzygium guineense</i>	Cu	228	246	42	146	1.07	0.59	0.64

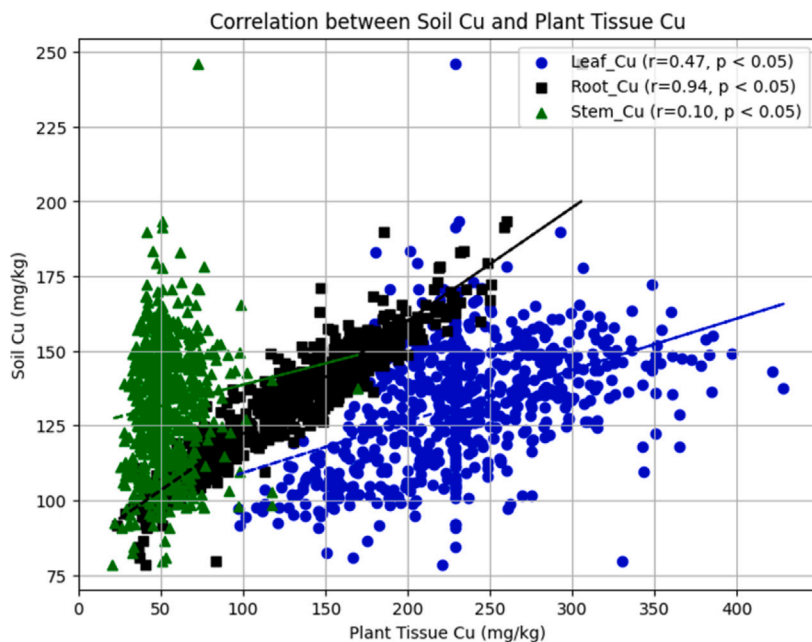


Fig. 2. Correlation between Cu content in soils and plant tissues at the Mitumba Cu-Co prospect.

higher in *A. angustifolium* (2.09), followed by *H. katangense* (1.68), and lastly *D. condilocarpon* (1.41) thus indicating these species are good Cu accumulators. In addition to Cu, *H. katangense* shows an even higher Co bioconcentration of 2.99 but its translocation and accumulation factors were very low (Table 4).

3.5. Geochemical anomaly detection in soil-plant systems

Exploratory data analysis (EDA) using median plus twice of the median absolute deviation (mad) indicated varying Cu thresholds in soils and the respective plant tissues (Table 5). The highest Cu threshold

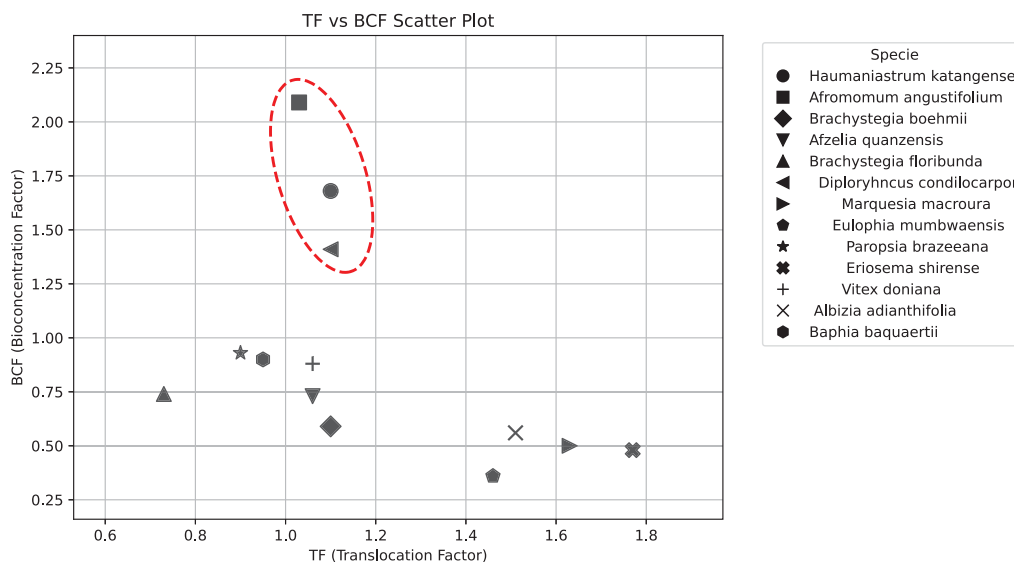


Fig. 3. Translocation and bioconcentration factors (TF and BCF) of native plants at the Mitumba Cu-Co prospect.

Table 5

Copper threshold values in soil and plant tissues in mg kg⁻¹.

Sample media	Median	MAD	Median + 2 MAD
Soil	134.3	14.5	163.2
Plant roots	127	39.4	205.8
Plant stems	51	8.3	67.6
Plant leaves	228.5	34.2	297

is shown by the leaves, followed by the roots, then the soils and lastly the stems.

Probability plots (Fig. 4) of the soil and plant tissue Cu at the Mitumba Cu-Co prospect indicated the presence of different distribution patterns and significant anomalous populations in both soil and plant tissues particularly leaves and roots. The Cu threshold values for soils and plant roots obtained using median + 2 mad were within the range of values that were graphically obtained using the probability plots. Plant roots and leaves have a wider distribution of Cu values that show enrichment as compared to the soils. This is further confirmed by box and whisker plots (Fig. 5) which show Cu anomalism in both soil and plant tissues of the Mitumba Cu-Co prospect. The box and whisker plots indicated the presence of significant populations of data in soils, roots, and leaves that demonstrate Cu enrichment while the plant stems generally showed a uniform distribution across the different quartiles of the phytochemical dataset. This is shown by the same mean value in the quartiles of the stem Cu data; mean value is shown by the central black box in the whisker plot (Fig. 4).

3.6. Significance of anomalism

The p-values obtained from the MWW test demonstrated that the on-mineralized and background samples of plant tissues had significant statistical differences in the Cu contents for plant roots and leaves. Plant roots and leaves had respective p-values of 0.03 and 0.01 that were less than the level of significance ($p < 0.05$) that resulted in the rejection of the null hypothesis. The p-value for the stems was 0.17 and, in this case, the null hypothesis was upheld suggesting the lack of significant differences in Cu contents of the on-mineralized and background stem samples.

3.7. Element uptake in soil-plant system

The prediction models for Cu transfer from the soil to the different plant tissues is shown in Fig. 6. The SMLR results indicated that Cu uptake was best predicted in soil-root systems with a high predictive power ($R^2 = 0.84$). The prediction of Cu uptake from the soil to the leaves showed a significant reduction in the coefficient of determination ($R^2 = 0.27$) and plant stems demonstrated poor prediction results with a negative coefficient of determination. The standard error associated with the prediction of Cu uptake in the plant tissues was; roots (0.069), stems (7.2), and leaves (0.075). In addition to soil Cu content, the physicochemical variables that significantly influenced model results in soil-plant systems were (in order): soil pH > soil organic matter > electrical conductivity > clay content. According to SOM (Fig. 7), Cu bioavailability in soils is significantly enhanced by a relatively low pH, organic matter and clay content. These soil physicochemical variables influenced Cu uptake by plants in the Mitumba Cu-Co prospect leading to a strong spatial correlation between soils and the plant roots. The SOM (Fig. 7) shows significant similarity between leaf Cu concentration and the soil electrical conductivity (EC) suggesting their directly proportional correlations. Stem Cu concentrations in the plant species are mainly influenced by pH and the content of organic matter in the soil.

4. Discussion

4.1. Vegetation associations in the Mitumba Cu-Co prospect

Most of the inventoried plants in the Mitumba Cu-Co prospect are trees of the Fabaceae family but among these species, only *B. boehmii* was associated with zones of high coating index (CoI) which is a measure of the density, frequency and surface area covered by a particular plant (Matanzas et al., 2021). Herbaceous species from different families were predominant in the study area as all of them were associated with CoI of 3–4. The distribution of these plant species and significant accumulation of Cu in their respective tissues indicates their adaptation capabilities to the soil Cu concentration of the study area. The Mitumba Cu-Co prospect area supports a diverse range of plant species because of the different bioavailable fractions of metals in the soil which may have formed from an interplay of several abiotic factors and chemical processes (Saad et al., 2012; Séleck et al., 2013). The native plants mapped in the study area are common in

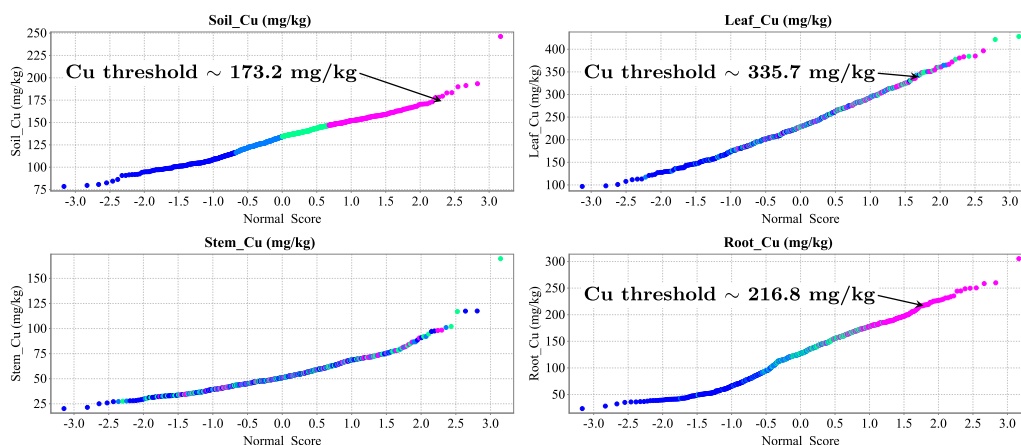


Fig. 4. Probability plots of soil and plant tissues at the Mitumba Cu-Co prospect.

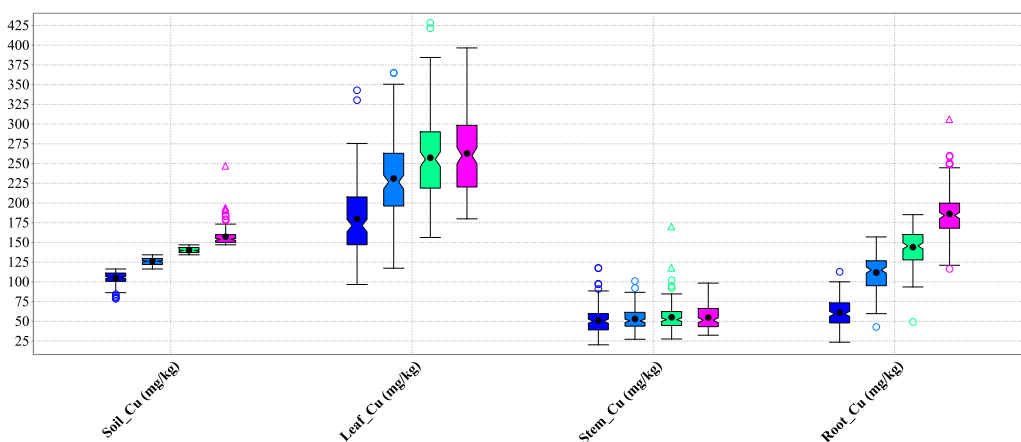


Fig. 5. Box and whisker plots of soil and plant tissue Cu in the study area. Cu values are attributed into quartiles for each of the sample media.

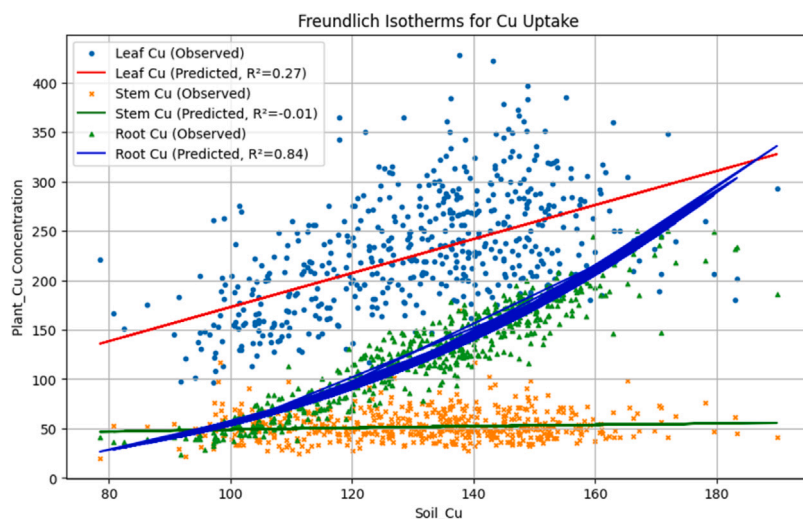


Fig. 6. Prediction models of Cu uptake in soil-plant systems of the Mitumba Cu-Co prospect. Metal concentration in both soils and plants are in mg kg^{-1} .

the ZCB and some of them have been observed to occur in mine generated wastelands and were previously screened as candidate species for ecological restoration (Festin et al., 2019b; Matakala et al., 2023). These species also have promising potential for phytogeochemical exploration (Mukube et al., 2024). Notable families from the Mitumba Cu-Co prospect that have been widely reported as metallophytes in

active mining areas of the ZCB include Fabaceae, Dipterocarpaceae, Lamiaceae (Boisson et al., 2016; Lange et al., 2016; Morrison et al., 1979). Based on the CoI, this study has identified *H. katangense* (Lamiaceae), *A. angustifolium* (Zingiberaceae), and *B. boehmii* (Fabaceae) as the most dominant native plant species in the Mitumba Cu-Co prospect (Table 2). Such dominance coupled with their occurrence on degraded

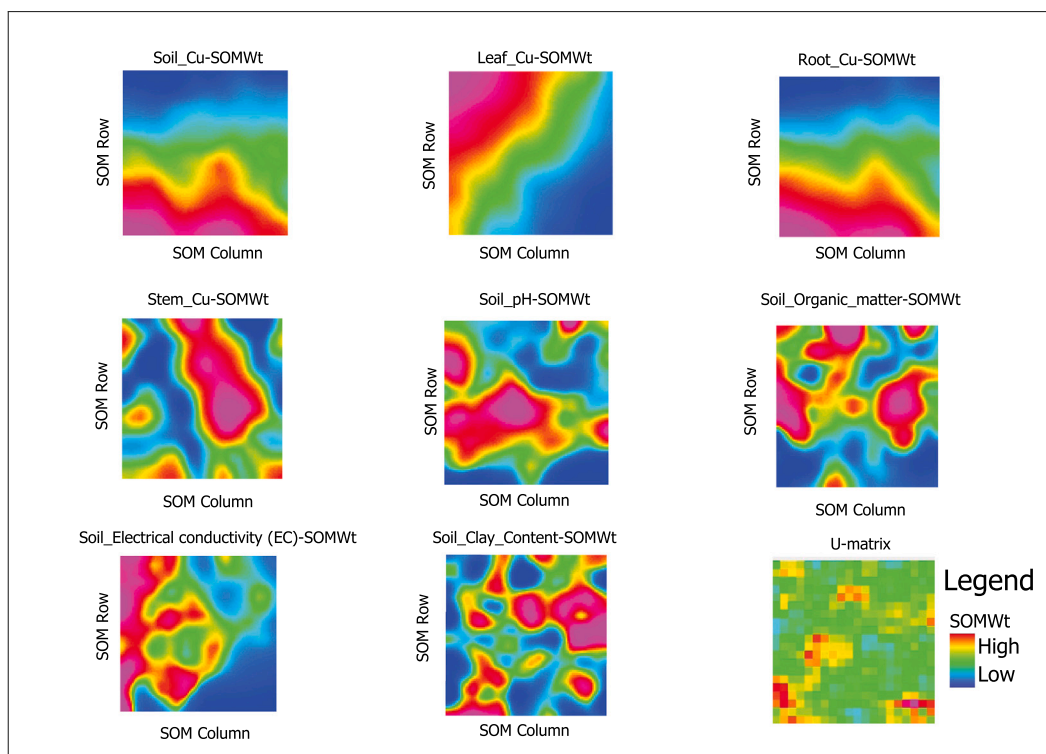


Fig. 7. Cu distribution patterns in plant tissues with respect to soil physicochemical parameters, pH, clay content, electrical conductivity, organic matter and soil Cu content. Unified distance matrix (U-matrix) represented a SOM in which a particular node has a U-matrix value that is equivalent to the average Euclidean distance between the weight vector of a given node with its nearest neighbors.

landscapes in the CACB suggests that they may be indicators of metal enriched environments (Alekseenko et al., 2021; Pollard et al., 2014). As such, they represent good candidate species for phytogeochemical sampling in mineral exploration. Additional species with a high CoI value are *A. quanzensis*, *B. floribunda*, *D. condilocarpon*, *M. macroua*, *E. mumbwaensis*, *P. brazeana*, *E. shirensis*, and *V. doniana*, indicating they could be considered for phytogeochemical exploration in the ZCB.

4.2. Phytogeochemical potential of identified plant species

In this study, most of the inventoried plants have $TF > 1$ indicating their ability to translocate Cu from the roots to the aboveground biomass but only three species have $BCF > 1$ and $TF > 1$ (Fig. 3). Moreover, these three species (*H. katangense*, *A. angustifolium*, and *D. condilocarpon*) effectively translocated bioavailable Cu from the soil to the plant leaves as shown by the $AF > 1$ (Table 4) thereby satisfying the requirements for plant suitability in mineral exploration. Several factors underpin the suitability of the selected plant species for phytogeochemical exploration of buried Cu-Co deposits in the Mitumba area. According to Nkoane et al. (2005), mineral deposit indicator plants accumulate significant fractions of bioavailable metals in the rhizosphere. Most importantly, *H. katangense* which was initially known as the copper flower that indicated buried mineral deposits (de Plaen et al., 1982) has been widely reported as a hyperaccumulator species that absorbs more than 5000 mg kg^{-1} Cu and 2000 mg kg^{-1} Co in its leaves particularly in the degraded landscapes of the CACB (Chileshe et al., 2020; Festin et al., 2019b; w. Ilunga et al., 2015). While the Cu and Co concentrations in the leaves of *H. katangense* in the Mitumba Cu-Co prospect are much lower than what has been reported as the threshold ($> 1000 \text{ mg kg}^{-1}$) for hyperaccumulation (Pollard et al., 2014), it still demonstrated a higher value of AF (Table 4) which is a critical requirement for species selection in phytogeochemical exploration targeting (Ouyang et al., 2024). Moreover, hyperaccumulation thresholds may have been determined based on plant samples growing on metal

contaminated soils from anthropogenic sources rather than geogenic processes. Unlike *H. katangense*, the species *A. Angustifolium* and *D. condilocarpon* have been scarcely investigated for metal accumulation and geobotanical indication of buried mineral deposits. However, their presence in forest ecosystems of metal enriched environments has been reported (Leteinturier et al., 2001) even though the factors causing their high frequency and significant BCF and TF remain unknown to date. The possible causes could be related to (i) better adaptation mechanisms supported by their physiological makeup, (ii) positive ecological interaction from a multi-element geochemical environment of the studied area in which certain elements may be enriched and depleted to promote growth of the plant species, and (iii) favorable geological and soil physico-chemical conditions that drive metal dispersion and enhance species abundance as well as Cu and Co accumulation in Mitumba prospect area. Additional research is required to address and confirm the above enumerated assumptions and provide insights into the major factors and mechanisms controlling the observed species richness and metal accumulation patterns across the study area.

4.3. Selection of phytogeochemical sample media

In addition to the selection of indicator plant species, it is important to choose and sample an appropriate plant organ for effective phytogeochemical exploration of mineral deposits. All the three selected species in the study area showed a higher Cu concentration in the leaves compared to the roots and stems (Table 4), which agrees with other studies that investigated metal accumulation in plants (Leitenmaier and Küpper, 2013; Rascio and Navari-Izzo, 2011). This further demonstrates the hyperaccumulation characteristics of the selected species and their potential use for phytogeochemical exploration targeting of buried ore deposits. Except for *D. condilocarpon* which showed an average Cu concentration of 120 mg kg^{-1} in the stems, the species *H. katangense* and *A. angustifolium* had less than the limits of detection ($< \text{LOD}$). The stems mainly function as pathways for nutrients and fluids from

the roots to the leaves through xylem and phloem vessels. A possible reason for the observed lower and < LOD Cu concentration in the stems could be due to their transport function which does not allow for Cu to accumulate but only enables its transport to the plant leaves for storage. Whereas leaves had higher Cu concentrations than roots in the study area, the overall correlation of root Cu concentration with the subsoil was much higher in the roots than the leaves (Fig. 2). We postulate that one of the contributing factors for a lower correlation between soil and plant leaves is the additional Cu in the leaf tissues that is received from other inputs (i.e., sucked up from mineral surfaces and groundwater sources) (de Plaen et al., 1982; Vela-Almeida et al., 2015). Baseline geochemical surveys in the ZCB indicate that metal anomalies in freely drained soils were transported from deeper horizons by vegetation (Govett, 2010; Tooms and Webb, 1961). This is supported by the fact that the three selected plant species have elevated Cu concentration in their leaves, and they are growing in soil of relatively low Cu concentration suggesting a possible secondary source of bioavailable Cu. Similar to observations from other studies (Asensio et al., 2018; Marrugo-Negrete et al., 2016), the root Cu concentration reflects the soil chemistry in the study area as demonstrated by the strong and significant correlation coefficient (0.94) between soil Cu and root Cu concentrations. This is because the roots have a direct exposure to bioavailable elements in the soil which sometimes tend to accumulate in the cell walls to avoid toxic effects such as necrosis and chlorosis in the leaves (Kumar et al., 2021; Shabbir et al., 2020). However, plant taxa may sometimes control the relationship between the content of Cu in the species and the soil Cu concentration. Exploratory data analysis by means of numerical and graphical approaches both showed the presence of significant Cu anomalism in plant roots and leaves. Plant leaves had a higher threshold Cu value than the roots, even though they showed a wider distribution of anomalous values (Fig. 4). Cu accumulation in the roots was observed to be plant specific and the most accumulation was associated with a relatively low metal content in the soil (Table 4). Analogous studies that sampled plant roots and leaf tissues for trace element indication of mineralized zones only selected the leaves as plant organs with strong and significant metal anomalism (Nkoane et al., 2005; Ouyang et al., 2024). Trace element anomalies in plant leaves indicating both soil contamination and natural enrichment from concealed orebodies has been reported in recent studies (Ouyang et al., 2024; Rathod et al., 2015). The possible reasons for the inability of previous studies to discriminate anomalies in plant roots could be (i) the limited number of plant species sampled for phytochemical screening, and (ii) the sampled plants may have had uniform metal tolerance characteristics while this study explored a diverse range of species with varying metal tolerance mechanisms. Therefore, we identified both plant roots and leaves as being essential sample media for successful phytochemical exploration targeting campaigns.

4.4. Factors controlling metal uptake in soil-plant systems

The major factors influencing metal uptake in plant species in the study area were constrained from a predictive model of Cu transfer in a soil-plant system that employed soil edaphic factors and the elemental composition of respective plant tissues as input variables. The best prediction results are shown by soil-root systems ($R^2 = 0.84$), and this confirmed the findings of the correlation analysis, highlighting soil Cu content, pH, and organic matter as the most significant variables influencing Cu concentration in plant roots. Similar prediction models with differences based on the selected soil variables and species types used have been developed by other researchers (Cipullo et al., 2019; Ding et al., 2014; Palansooriya et al., 2022). Most of the models identified metal content, soil pH, organic matter, and clay content as the major controlling factors of trace element uptake in soil-plant systems. These Freundlich type soil-plant metal transfer models offer

competitive advantages due to their simplicity and can easily be applied in the real world.

Advances in machine learning techniques have created a platform for developing predictive models of element uptake in soil-plant systems that are not affected by environmental pollution. The artificial neural network employed by SOM also underscored the significant influence of soil Cu content, pH, organic matter, and clay content in metal uptake for the investigated soil-plant system. The SOM (Fig. 7) highlight that zones of elevated Cu concentration in plant tissues particularly roots and leaves are associated with low values of pH, organic matter and clay content. Low pH or acidic soils have been shown to stimulate metal uptake by plants with significant enrichment in aboveground plant biomass (Bravo et al., 2017). The low organic matter and clay content enhances metal bioavailability and thus, improved Cu uptake in plants.

5. Limitations of the study

Whereas this study shows promising potential for the use of phyto-geochemistry in mineral exploration based on Cu and Co accumulation in plant tissues of selected native species, several limitations still need to be addressed. We enumerate some of these limitations as follows:

1. Certain plants, especially herbaceous species, are usually ephemeral and may not be available for sampling throughout the year.
2. Seasonal variations and fluctuations in the groundwater table may affect the concentration of elements in plant tissues. Therefore, future research should consider the identification of immobile trace elements in plant tissues that provide a consistent geochemical signal to fingerprint mineralized zones.
3. Plant species are prone to contamination in brownfield or near-mine exploration sites due to windblown dust and other surficial local transport processes. As such, it may be challenging to identify positive and significant phytochemical anomalies related to buried mineralized zones.

6. Conclusion

This study demonstrated the potential of phytochemical exploration based on the ability of autochthonous plants to accumulate Cu and Co in their respective tissues. The results revealed the presence of a diverse floristic composition comprising native tree and herbaceous species from 12 different families suggesting a great opportunity for selecting optimal plant species that may be useful in phytochemical exploration targeting of concealed orebodies. Three species from different families including *Haumaniastrum katangense* (Lamiaceae), *Aframomum angustifolium* (Zingiberaceae), and *Brachystegia boehmii* (Fabaceae) were identified as the most important and predominant species based on their coating index in the study area. Other species with a relatively high coating index and thus, generally predominant in the study area are *Afzelia quanzensis*, *Brachystegia floribunda*, *Diplorynchus condilocarpus*, *Marquesia macroura*, *Eulophia mumbwaensis*, *Paropsia brazeana*, *Eriosema shirensis*, and *Vitex doniana*. Such a wide pool of species increased the probability of identifying plant species indicative of mineralized zones. Element accumulation patterns varied amongst different plant species in the study area. Cu accumulated in all the leaves and most of root organs of the inventoried plant species in the study area while Co was only observed in the root and leaves of *Haumaniastrum katangense* and *Aframomum angustifolium*. Most of the species' stem samples had very low metal concentrations which in some species was below the limit of detection, < LOD. Cu was easily translocated from the roots of most plant species to their aboveground biomass as shown by their translocation factors ($TF > 1$) but only three species were able to sequester significant amounts of Cu from the rhizosphere. These species namely, *Haumaniastrum katangense*, *Aframomum angustifolium*,

and *Diplorynchus condilocarpon* were characterized by translocation and bioconcentration factors (TF and BCF) > 1 thus, making them the best suited candidate species for phytogeochemical exploration in the Zambian Copperbelt. In addition, these species had an accumulation factor (AF) > 1 which is a critical requirement of species selection for phytogeochemical exploration. The Cu content of plant leaves in the identified species showed moderate correlation with the soil Cu content while the root Cu concentrations were significant. Predictive modeling of element uptake in the soil-plant ecosystem using stepwise multiple linear regression showed the best prediction results in the soil-root system, and the possible soil variables that mainly influenced model results were pH, organic matter and the soil Cu content. This was further demonstrated by SOM, an artificial neural network which highlighted low pH, low clay content and organic matter as the major soil variables driving Cu bioavailability and uptake in the study area. The current study provides the foundation towards identification of plant species and useful tissues for phytogeochemical exploration of concealed orebodies in the Zambian Copperbelt. Further, by revealing the Cu and Co accumulation patterns of the identified indicator plants, this study forms the basis to advance research related to phytogeochemistry in the region, with further research expected to shift towards identification of multi-element geochemical patterns and spatial anomaly detection in the identified species.

CRediT authorship contribution statement

Pumulo Mukube: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Stephen Syampungani:** Writing – review & editing, Supervision. **Lerato Machogo-Phao:** Writing – review & editing, Supervision. **Murray Hitzman:** Writing – review & editing, Supervision.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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