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Review

Geochemistry of Terrestrial Plants in the Central African Copperbelt: Implications for Sediment Hosted Copper-Cobalt Exploration

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Abstract: Mineral exploration has increasingly targeted areas covered by in situ or transported overburden for shallow to deep-seated orebodies. It remains critical to develop better means to detect the surficial chemical footprint of mineralized areas covered by thick regolith. In such settings, plant geochemistry could potentially be a useful exploration tool, as different plant species have varying degrees of tolerance to metal enrichment in the soil. This review provides insights into the geological and geochemical controls on metal accumulation patterns in soil–plant systems of the Central African Copperbelt. In addition, it highlights the opportunities for integrating the geochemistry of terrestrial plants in emerging exploration technologies, identifies research gaps, and suggests future directions for developing phytogeochemical sampling techniques. This review was conducted using reputable online scholarly databases targeting original research articles published between January 2005 and March 2023, from which selected articles were identified, screened, and used to explore current advances, opportunities, and future directions for the use of plant geochemistry in sediment hosted Cu–Co exploration in the Central African Copperbelt. Various plant species are recognized as ore deposit indicators through either independent phytogeochemistry or complementary approaches. In the Central African Copperbelt, the successful application of hyperaccumulator species for phytoremediation provides the basis for adopting phytogeochemistry in mineral exploration. Furthermore, current advances in remote sensing, machine learning, and deep learning techniques could enable multi-source data integration and allow for the integration of phytogeochemistry.

Keywords: phytogeochemistry; hyperaccumulators; mineral exploration; sediment hosted copper; machine learning; Central African Copperbelt

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1. Introduction

The Central African Copperbelt (CACB) is a world class metallogenic province of sediment hosted Cu–Co deposits that straddles the international boundary between Zambia and the Democratic Republic of Congo (DRC). Since its international discovery in the early 1900's, various surficial geochemical media including soils, termitaria, stream sediments and rock chips have been used in mineral exploration targeting [1,2]. Current mineral exploration is increasingly targeting areas covered by in situ or transported overburden for shallow to deep seated orebodies. Exploration in such terrains is extremely costly and challenging due to the suppression of mineralized rock signatures arising from thick regolith profiles. It remains critical to identify and select surficial media that provide useful vectors to mineralized zones.

Deep rooted phreatophyte shrubs and trees that are tolerant to elevated soil metal concentrations have become a source of growing interest for exploration and environmental geochemical research across the world [3–6]. Attempts to use plants as sample media in mineral prospecting date back to the mid-19th century [7], even though plant geochemistry was previously limited by analytical technology and the lack of statistical rigor in the interpretation of phytogeochemical data. However, plant geochemistry has recently been used in combination with other surficial media to detect metal anomalies related to ore deposits [8–10]. Such phytogeochemistry has been observed to effectively define anomalies related to mineralized zones from deeper sources over a number of ore deposits around the world including; the Kangerluarsuk zinc-lead-silver (Zn-Pb-Ag) deposit in Greenland [5], the Twin Lakes gold (Au) deposit in Canada [10], and iron-oxide-copper-gold (IOCG) mineral systems of the southern Olympic Domain, Australia [11].

The application of plant media in mineral exploration has been possible because of the numerous response patterns demonstrated by plant species in relation to elevated metal concentrations in soils. Most plant species display sensitivity to high metal concentrations and others show tolerance and accumulate metals in their roots and/or their aboveground organs, such as shoots, flowers, stems, and leaves. In the CACB, cuprophytes and cobaltophytes are present and represent a diverse range of plant species that could potentially be useful in the application of phytogeochemistry in mineral exploration target generation [12,13]. These species include both hyperaccumulators that are useful in phytoremediation [14] and excluders that are related to phytostabilization [15]. Indicator plant species have been described as those that are consistently confined to a narrow and distinctive environmental range [16], and thus, may be associated with spatially restricted mineralized zones. However, the independent geological and phytogeochemistry variables linked to plant community diversity and assemblages remain unclear.

This review seeks to (i) insightfully discuss the geological and geochemical controls on metal accumulation patterns in soil–plant systems in the Central African Copperbelt; (ii) highlight the potential opportunities for integrating the geochemistry of terrestrial plants in emerging mineral exploration technologies and data integration approaches; and (iii) identify research gaps and suggest further directions for developing phytogeochemistry as a sampling technique in mineral exploration.

2. Methodology

This review was conducted using the guidelines of preferred items for reporting systematic reviews and meta-analyses (PRISMA) [17,18] (Figure 1) through reputable online scientific databases. The literature databases searched in this study included Google Scholar, Web of Science, Science Direct, and Springer. This literature search included articles addressing the geochemistry of terrestrial plants in the CACB and its implications on sediment-hosted Cu–Co exploration. We restricted our search to original research written in English, from articles published mainly between January 2005 and March 2023 to identify the "gold standard", and recent literature on plant geochemistry with a focus on Cu–Co tolerant plant species.

The PRISMA approach generated a total of 1758 studies from the online databases and 34 studies from other sources. Following the removal of 1008 duplicates, 784 studies were retained. Ultimately, a total of 165 and 79 studies were selected to conduct qualitative and quantitative synthesis, respectively. While this literature review considered a global perspective, we scaled down the search to the tropical and sub-tropical environments as similarities in climatic conditions may support similar plant species and may also have analogous ore deposits. To filter literature for analysis, we conducted a search on article title, abstract and keywords using key terms such as "phytogeochemistry", "biogeochemistry", "plant geochemistry", "phytoexploration", "hyperaccumulator", "excluders", "indicator species", "sediment hosted copper deposits", "Central African Copperbelt" (including singular and plural forms of these words). Table 1 provides a summary of the search string combinations used in extracting relevant articles for respective review components and further processing.

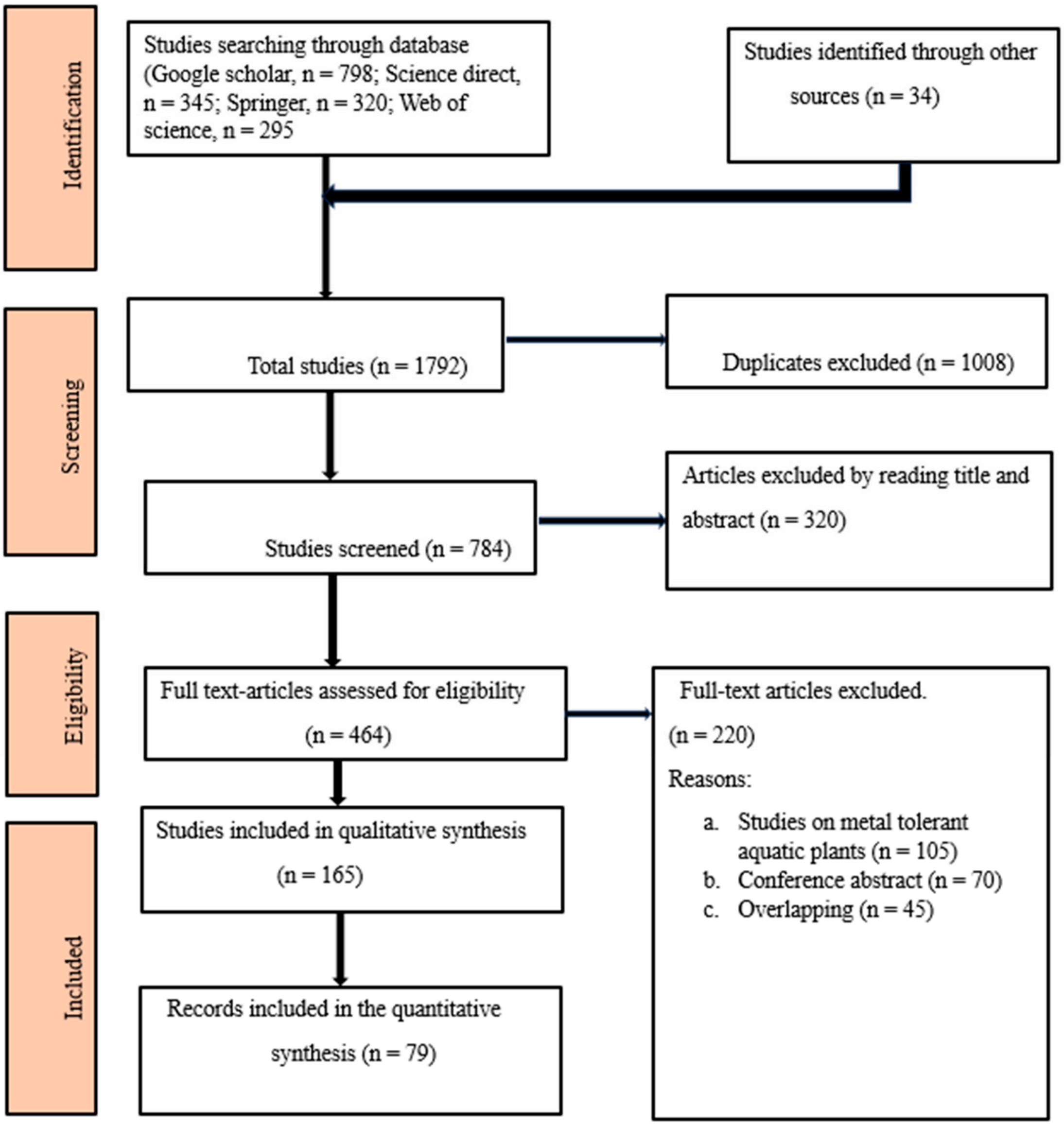

Figure 1. PRISMA flow chart used in identification, screening, and inclusion of literature in this study.

A full text assessment was performed to exclude studies regarding aquatic plant species, conference abstracts, and overlapping studies. As for quantitative synthesis, we considered soils sampled from the B-horizon (30–60 cm) and plant samples from both contaminated and non-contaminated sites were included in the review. To avoid bias during the initial search stage and to maximize the extraction of articles with a global reach, we independently searched the digital databases using search terms with slightly varying synonyms. This was followed by a cross-examination of the search results where the same filter criteria were used to specify the period, document type, region, and the field of study. In the second stage, the extracted article metadata were verified for completeness and originality. The articles that met the quality assurance process were included for further synthesis.

Table 1. Key search string combinations used to extract articles for the respective review components and further processing.

Research Component	Addressed in Section	Search String
1. Geological and Geochemical controls on plant species distribution in Cu–Co mineralized sites	Section 3.1: Section 3.3	[[[All: geological] AND [All: phytogeochemistry]] OR [[All: plants] AND [All: geology]] OR [[All: soil] AND [All: metal]] AND [[[All: Anomalies] AND [All: Central African Copperbelt]] AND [All subjects: Exploration and Environmental Geosciences] AND [All subjects: Ecology- Environmental studies] AND [All subjects: Environmental studies] AND [Article Type: Article] AND [Language: English] AND [Publication Date: (1 January 2005 to 31 March 2023)]
2. Use of metal tolerant plants as ore deposit indicators	Section 3.4: Section 3.5	[[All: "terrestrial plants"] OR [All: "plants"]] AND [[All: "metallophyte"] OR [All: "indicator]] AND [[All: "hyperaccumulator"] AND [All: "metal"] AND [All: "mining"] OR [All: "exploration"] AND [All: "environmental"] AND [Language: "English"]
3. Emerging phytogeochemistry integrative mineral exploration technologies	Section 4.2	[[All: "plants"] OR [All: "mineral exploration"]] AND [[All: "prospecting] OR [All: "emerging"]] AND [All: "technologies"]] OR [All: "Remote]] OR [All: "Sensing"]] OR [All: "GIS"]] OR [All: "machine learning"]] AND [All: "deep learning"]] AND [All: "metallophyte"]] AND [Language: "English"]

The results from the search engines and databases were downloaded and imported into Mendeley reference manager version 1.19.8. The pertinent metadata was checked and sometimes updated for each article including the title, author list, publication year and month, volume, page numbers, DOI if available, abstract, and keywords. However, articles that were missing the relevant metadata such as author, title, and publication year were also removed from the list of useful articles in this review. In addition, manual removal was conducted to ensure the completeness and relevance of the articles that were included in the review process [18].

A bibliometric analysis was conducted to classify articles with respect to the publication year, authors, region, main objective(s), metallophyte types, and approaches used for the classification of metal tolerant plant species. Based on the PRISMA filtering protocol and the subsequent number of articles included in this study, there is a notable increase in studies focusing on metal tolerant plant species associated with either contamination or natural hyperaccumulation in the CACB (Figure 2). This suggests a growing interest in the incorporation of metallophytes and the use of a geochemical footprint of terrestrial plants in mineral prospecting.

A general overview of publications during the review period suggests that most of the studies conducted on the geochemistry of terrestrial plants in the CACB are from the DRC and Cu–Co tolerant plants are globally recognized as having first been recorded from the mineralized Katanga outcrops of the southern DRC [19–21]. However, most of these studies are biased towards ecological restoration research and plant species characterization as either being useful for phytoremediation or phytostabilization and therefore, provide potential for application in the phytogeochemical exploration of ore deposits.

Furthermore, studies from the tropics, particularly Australia, Brazil, and Botswana show that various plant organs (roots, stems and foliage) can be used in identifying indicator and pathfinder elements associated with mineralized zones [11,22–25]. From the examined literature, most researchers focused on the use of plant geochemistry for the exploration of Au, Cu, Ni, Pb, Zn, and U. All these elements are associated with sediment hosted Cu–Co deposits, such as the CACB [26], even though some earlier studies suggest that most plant analyses in this region were conducted on contaminated material and that, whilst still hyperaccumulating Cu-Co, the true extent of this phenomenon remains unclear [21,27].

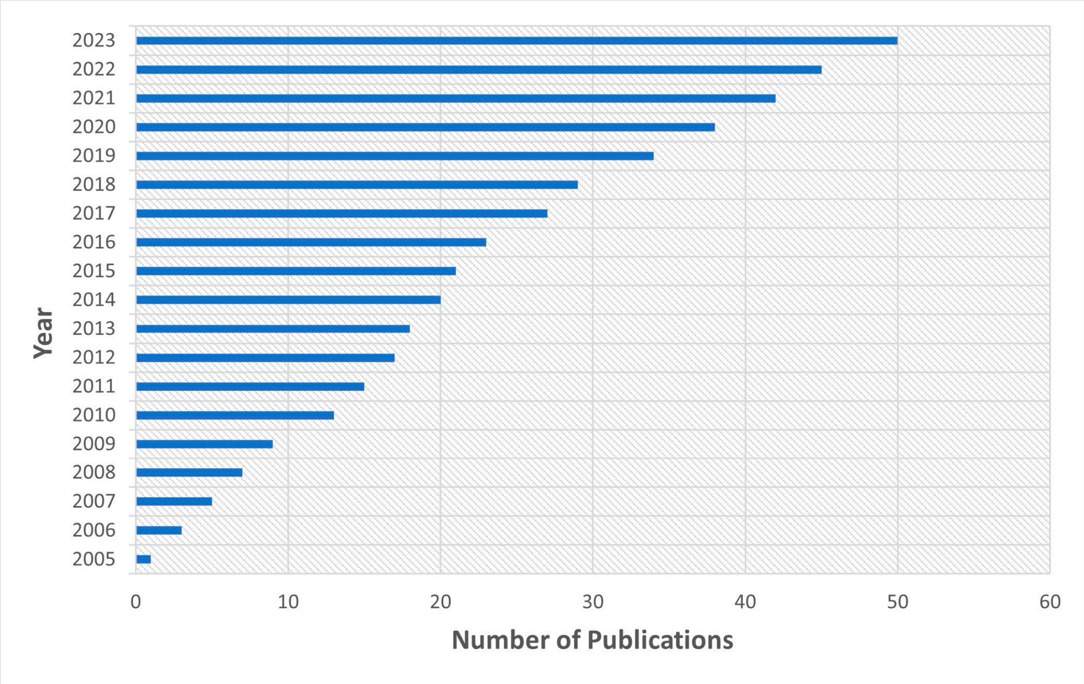

Figure 2. Distribution of research publications on metal tolerant plant species in the Central African Copperbelt.

Nonetheless, current advances in elemental and mineralogical analytical techniques, including the use of the scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) and the synchroton X-ray absorption spectroscopy (XAS), provides the opportunity to determine the contribution of potential surficial contamination to internal Cu and Co concentrations in the plant material [28]. This provides the basis for integrating the geochemistry of terrestrial plants in Cu–Co exploration. Furthermore, the rapidly growing global interest for low impact and environmentally friendly exploration technologies highlights the need to employ surficial geochemical soil and plant sampling in the definition of mineral exploration targets [29]. The data obtained via their application can be useful in constraining regional and local scale geological models which help in understanding geological processes and locating deep-seated mineral deposits with minimal environmental impact. However, studies have also revealed the existing weak linkages among geochemical, geological, and the relevant phytogeochemical variables required for mapping concealed mineralized rocks over spatiotemporal scales [30,31]. As such, the reviewed articles have enabled the conceptualization of factors underpinning the relationship between terrestrial plants and the underlying geology including the criteria for selection of metal tolerant plant species in the geochemical environment.

3. Spatial Trends of Geological and Geochemical Controls on Plant Species Characterisation and Distribution

3.1. Geologic Setting of the Central African Copperbelt

The Central African Copperbelt is one of the largest economic copper accumulations in the Earth's crust and is a principal contributor to the global copper and cobalt inventory [26,32]. Several worldclass ore deposits, including the high grade Zambian Copperbelt (ZCB), Congolese Copperbelt (CCB) and the low grade but high tonnage deposits in the Domes region of northwestern Zambia, are exploited from the Central African Copperbelt [33] (Figure 3). In addition, it is an important source of other metals including Ag, Pb, Zn, and may also contain significant germanium (Ge), Au, Ni, platinum group elements and rhenium (Re) [34,35]. The ore deposits of the CACB are hosted within the northwest-southeast (NW-SE) trending sedimentary rocks of the Neoproterozoic Katangan Supergroup [36–38]. A wide range of host rocks, including clastic and carbonate rocks, are present in the CACB. These rocks were deposited in a series of extensional sub-basins within the broad Katanga basin which formed as part of the Rhodinian supercontinent breakup [39,40]. While lithostratigraphic sequences have similarities on a regional scale within the Katanga basin, individual depocenters had distinctive features, especially with regard to basal successions [38,41]. As such, the Neoproterozoic Katangan Supergroup lithological units show spatial variations. The estimated maximum thickness of the Katanga sequence is thought to be approximately 5–10 km in the Congolese portion of the basin [37,42].

Although most studies subdivide the Katangan Supergroup into three main sequences [26,41,43], recently completed lithostratigraphic revision and sedimentary evolution suggest four subgroups of the Katangan stratigraphy, i.e., (from bottom to top of the basin) the Roan, Nguba, Kundelungu, and Biano Groups [40] (Figure 4). This subdvision is based on the presence of two regional markers formed by two globally significant glacially related diamictite units of Sturnian and Marinoan age, the Mwale, and Kyandamu subgroups at the base of the Nguba and Kundelugu groups, respectively [44]. The lithofacies associated with these diamictite intervals indicate a wide range of depositional regimes including glaciogenic, glaciomarine, glaciofluvial, glaciolucustrine and mass flows [40,45].

There is an extensive body of literature providing insight into the metallogenic processes that operates within the CACB [36,41,46–48]. Mineralized host rocks within the ZCB and the Domes region of the northwestern Zambia include the lower Katangan Supergroup strata (Roan and Nguba groups) and basement rocks just below the Katangan unconformity. In the CCB, significant deposits are concentrated in the Roan and Nguba groups with smaller deposits in Kundelungu Group rocks. Most studies suggest continuous but multi-staged Cu–Co mineralization extending from the initial period of rift related sedimentation at about 815 Ma [42] to a late orogenic stage of mineralization from between 580–500 Ma [49,50]. The source of the metals and significant mineral endowment remains unclear, but there is a general consensus that metals were sourced from both the basal red bed siliciclastic sediments of the Roan Group as well as from basement rocks [36,41,49,50]. Most of the district's ore deposits occur proximal to large regional structural features, such as originally synsedimentary normal faults or large anticlinal structures associated with basin inversion [38,40,51]. These structures could be conduits for mineralized fluid migration and may potentially make metals available for uptake by plant species from groundwater and soils.

Exploration Targeting in the Central African Copperbelt

The primary means of discovery in the CACB have been geological mapping to identify outcropping zones of mineralization, most of which were identified by local peoples long before the arrival of European explorers, and geochemical exploration. A number of geochemical techniques have been employed in mineral exploration. A wide range of media have been targeted for sampling including soils, termitaria, and rock chips [52–55]. Over the past several decades, geochemical exploration has moved from analyses primarily for copper to multi-element and isotopic analyses. These modern data sets enable not only the direct detection of subcropping mineralized systems, but also allow for the definition of broader zones of hydrothermal alteration as well as the potential to map the underlying bedrock lithology [56,57]. In addition, recent studies have used multi-source geochemical data sets in predictive geochemical mapping by employing machine learning and deep learning algorithms in geochemical data visualization and interpretation [58–61]. This provides an opportunity for the integration of phytogeochemical data in geochemical exploration.

While various geophysical methods have been used for lithostratigraphic and structural mapping in the CACB, the orebodies have proved to be poor geophysical targets. This is because they are generally not massive sulfides and are non-magnetic and, thus, cannot be targeted using electromagnetic (EM) and airborne magnetic methods [62]. Induced polarization (IP) and self-potential (SP) methods have only had limited success, even though the orebodies are characterized by disseminated sulfides [63]. This may be because of the vast areas containing disseminated sulfides which makes it difficult to reliably separate signal for areas containing dominantly copper sulfides. Phytogeochemistry may be a means of improving exploration success.

3.2. Phytogeographic Setting of the Central African Copperbelt

The presence of a wide range of lithological units within the Katangan Supergroup suggests the occurrence of a heterogeneous weathered zone and, thus, broad chemical makeup within the Katangan basin that may support growth of a variety of plant species including those that are useful for phytogeochemistry. The area underlain by Katangan strata is mainly characterized by the Miombo vegetation type (Figure 3), which has a wide range of plant species, thus, suggesting potential for species selection related to phytogeochemical exploration. The Miombo is a predominant vegetation formation in Central and Southern Africa with about 650 species being endemic to this region [21]. Among these plant species, 57 are absolute metallophytes that occur exclusively on Cu–Co enriched soils [64] and 23 are facultative metallophytes with over 75% of known plant populations occurring on Cu–Co rich soils [65,66]. The distribution of vegetation in the CACB is related to the form and concentration of bioavailable Cu and Co as well as an interplay of several chemical factors [67,68]. Plant species diversity is influenced by a range of Cu and Co chemical fractions in the soil that either increase or decrease metal bioavailabity [65]. Soil metal anomalies in mineralized areas result from the weathering of Katangan rocks with naturally elevated Cu and Co concentrations. The process of soil formation is mainly driven by both physical and chemical alteration of the parent rock material, and these alteration processes can be summarized as dissolution, hydration, hydrolysis, oxidation, reduction and carbonation [69,70]. The Cu and Co species are released from the parent rockmass and distributed in different soil phases, namely; solid, colloidal, and soluble soil phases depending on characteristic soil properties such as pH, organic matter content, metal concentrations, and redox conditions [71,72].

In southern DRC, Ilunga et al. [21] highlights that Cu–Co outcrops provide a variety of habitats according to the spatial variation of edaphic conditions, including the natural Cu–Co concentration. These mineralized outcrops form isolated and scattered hills in a landscape matrix of Miombo woodland [66]. In the Domes region of northwestern Zambia, several Cu accumulating taxa and hyperaccumulators were identified at the Kansanshi Cu outcrop despite mineral exploitation dating back to the early 20th century in the area [73]. At outcrop scale, soil Cu and Co concentrations primarily control plant species richness with soils resulting from high grade Cu–Co outcrops supporting the lowest total plant species richness [67,68]. However, on a regional scale, the spatial configuration of mineralized outcrops influences the plant species richness of Cu–Co endemics.

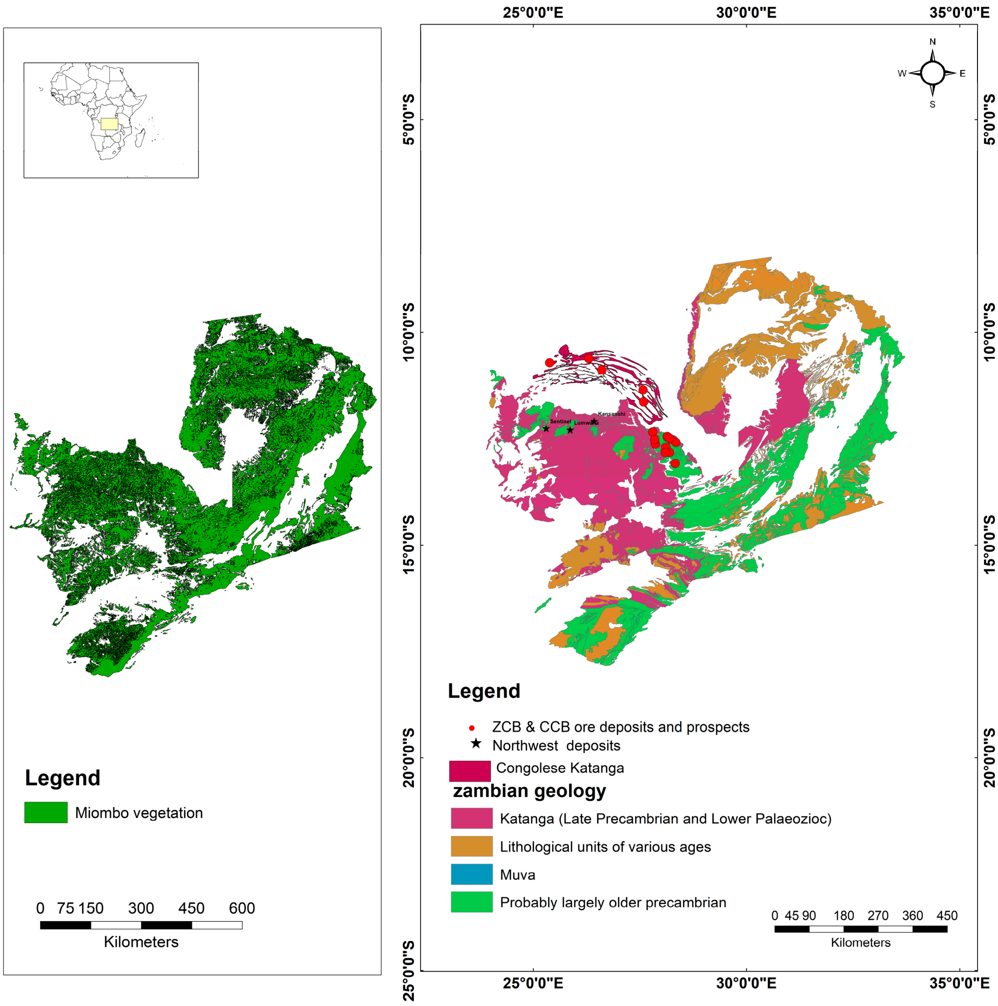

Figure 3. Geological and Vegetation map of Zambia and Southern Democratic Republic of Congo (DRC). Redrawn from Geology and Vegetation maps of Zambia [74,75].

Congolese Copperbelt					Zambian Copperbelt				Generalised rock units
Member	Formation	Subgroup	Group	Supergroup	Group	Subgroup	Formation	Member	
Petit Conglomerate		Biano	Kundelungu	~ 540 Ma	Kundelungu			Petit Conglomerate	Red arkose, conglomerate, shale
		Ngule							Dolomitic sandstone
	Kyandamu	Gombela		~ 635 Ma					Glacial diamictite
Grand Conglomerate		Bunkeya	Nguba		Nguba			Grand Conglomerate	Shallow marine carbonate
	Mwale	Muombe		~ 740 Ma					Glacial diamictite
		Mwashya	Roan	Katangan	Roan	Mwashya			Shale and siltstone
	Kansuki	Dipeta				Upper Roan			Argillaceous and dolomitic sandstone
	Mofya								
	R.G.S								
	Kambove	Mines							
	Dolomitic shales (S.D)								
	Kamoto								
		R.A.T				Lower Roan	Kitwe	Copperbelt Orebody	Terrigenous sandstone and conglomerate
				< 880 Ma			Mindola clastics		
				Basement	Basement				Basement

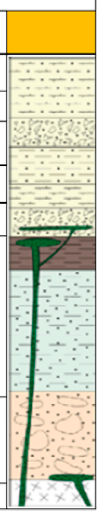

Figure 4. Lithostratigraphy of the Central African Copperbelt, compiled from [40,43]. The R.A.T unit represents the Roches Argilo–Talqueuses Formation. The gabbros crosscut the basement, lower Roan, upper Roan and Mwashya subgroups and are sometimes concordant to the strata.

3.3. Mineralisation and Trace Element Geochemistry

Typical Cu–Co ore minerals in the CACB include chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), carrollite (Co_2CuS_4), chalcocite (Cu_2S), heterogenite [CoO(OH)] and malachite [$CuCO_3(OH)_2$]. These minerals are usually disseminated along bedding planes and occur in nodules or as vein and fracture fillings in both clastic and carbonate host rocks [40]. Most deposits in the CACB contain, primary (hypogene) pyrite, chalcopyrite, bornite, chalcocite, and carrollite, with the latter three being generally the most important ore minerals [76]. Galena, sphalerite, pyrite, and pyrrhotite are commonly present at the peripheries of Cu–Co deposits, representing Pb–Zn–Fe halos which are a common feature of sediment hosted Cu–Co deposits [77,78]. Whole rock geochemical studies of sediment hosted stratiform copper deposits demonstrate a geochemical association of Cu-As-Ni-V-Mo-Bi ± Pb, Zn, U, Co with most being trace constituents of the dominant Cu–Co sulfides [52,79,80]. A number of deposits in Zambia are associated with potassic alteration. However, some deposits, such as the Kansanshi and Frontier, have a sodic alteration assemblage while most Congolese deposits tend to have a magnesian alteration signature [72].

Supergene alteration has been important in the CACB. Much of the chalcocite in the Central African Copperbelt is likely to have a supergene origin and in the CCB, and historically in the ZCB, much of the copper production came from copper carbonates such as malachite and copper oxides [42]. The most common copper bearing minerals characterizing the supergene zone are chalcocite, malachite, and chrysocolla with heterogenite forming the most important cobalt supergene mineral [81]. In addition to these, other secondary Cu–Co minerals are commonly present including native copper, cuprite, tenorite, azurite, libethenite, pseudomalachite, spherocobaltite, and cobaltoan carbonate [52,72].

Supergene altered and mineralized rocks are best known in the shallow subsurface but have been recognized to depths of >1 km [36]. However, most of the economic deposits associated with supergene mineralization occur at depths < 100 m and they show a depth profile mineral zonation characteristic of supergene deposits [33]. According to De Putter et al. [82], this depth profile zonation is characterized by a surficial leached zone composed of mainly hematite overlying an oxide enriched zone which is predominantly malachite in carbonate hosted deposits and chrysocolla in siliciclastic host rocks. Below this is a mixed/transition zone with the co-existence of supergene oxide and sulfide minerals which grades downwards into a sulfide rich zone (Figure 5).

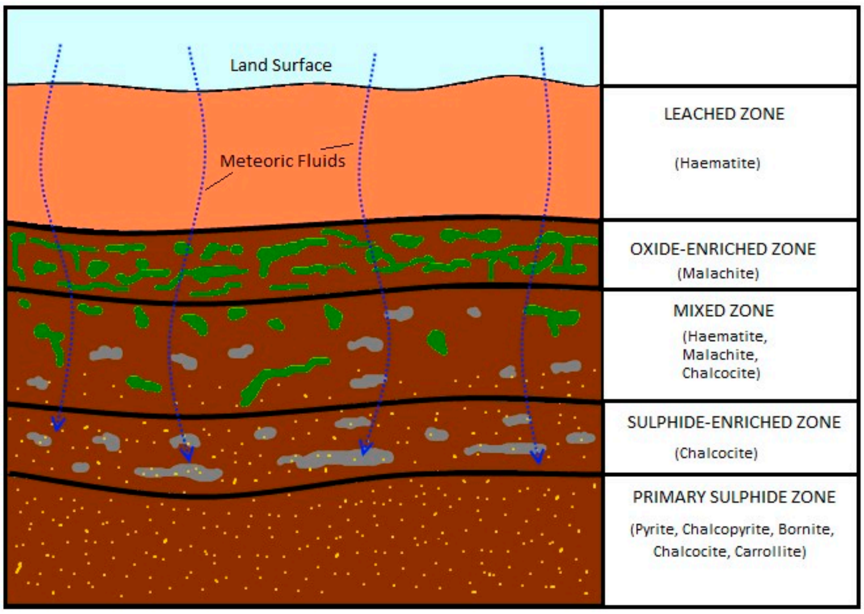

Figure 5. Generalized conceptual illustration of depth profile zonation of supergene mineralization in the Central African Copperbelt, displaying various alteration zones as well as their dominant ore mineralogy. Adapted from De Putter et al. [82].

The supergene enrichment mineralization process is initiated by the reaction of hypogene sulfide minerals with very low salinity and highly oxygenated meteoric fluids at low temperature (<30 °C). Dissolution of atmospheric carbon dioxide in rainwater generates dilute carbonic acid (H_2CO_3) which reacts with pyrite (FeS_2) and Cu–Co sulfides. The reaction increases the acidity of the meteoric fluid and improves its capacity to cause more supergene alteration [52]. Precipitation of supergene ores is primarily controlled by a significant drop in the redox potential (Eh) which frequently happens on top of the poorly oxygenated water table. As such, the oxide ore zone usually occurs at the base of the vadose (unsaturated) zone. The transition/mixed zone occurs in between and usually associated with fluctuations in the groundwater table [33]. However, the present-day water table may not correlate with the position of the paleo-phreatic zones which existed at the time of formation of these supergene orebodies.

3.4. Geochemical Controls on Metal Behavior in Terrestrial Plant Systems

The main interactive biotic and abiotic processes that control metal behavior in soil-plant systems are shown in Figure 6. Soils are the geochemical sink for trace elements and metal ions undergo a series of reactions in both solid and aqueous media, which vary over spatiotemporal scales [83,84]. As such, soil chemistry is dynamic and influenced by multiphase equilibria involving; (a) the solid phase, i.e., the phyllosillicates including clay minerals such as kaolinite, illite, smectite, etc., and hydrous oxides that include hydrous Mn, Fe and Al oxides, and the particulate organic matter (OM); and (b) the aqueous phase composed of water and dissolved constituents such as free metal ions, complexed ions, dissolved organic carbon (DOC), and other ligands.

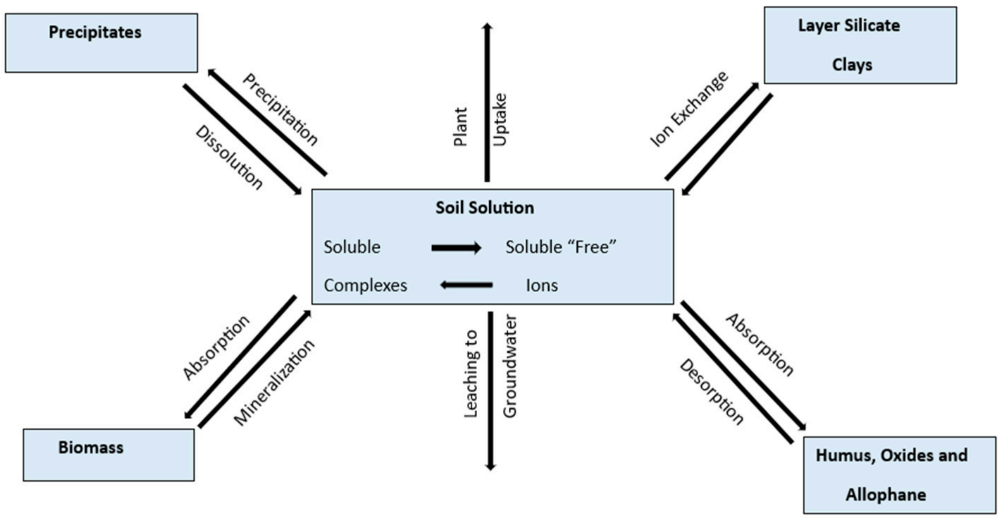

Figure 6. Key interactive processes in soil-plant systems affecting partitioning of trace metals.

From Figure 6, the major processes that govern metal behavior in soil–plant systems include ion exchange (adsorption–desorption), solubilization (precipitation-dissolution) and absorption (assimilation or immobilization) by living biomass. Microorganisms and plant roots interact with the soil dissolved species, and microbial and root exudates can affect the solubility and ultimate transport of the resulting compounds [85]. Essentially, these processes strongly influence the biogeochemical speciation of elements and control their solubility, mobility, bioavailability and metal enrichment in plants [19,80,86,87]. Furthermore, biogeochemical processes are driven by a few major variables such as pH, Eh, and cation exchange capacity (CEC) and these play a pivotal role in the mobility and bioaccumulation of elements in plants [83]. However, these are not exclusive variables as there are other biogeochemical and environmental factors that may influence phytogeochemical processes, element mobility, and bioaccumulation.

Generally, the retention capacity of soils for trace metals increases with an increasing pH. Bravo et al. [88] highlight that the bioavailability of Cu, Co, Zn, Ni, and Pb is significantly reduced in alkaline soils. As such, acidic soils tend to promote metal uptake by plants and metal enrichment in aboveground plant organs may be significantly higher than normal. pH underpins several driving factors of biogeochemical processes as it can affect the surface charge of layer silicate clays, OM and oxides of Fe, Mn and Al [52,72]. In addition to its effect on the sorption of cations and complexation with OM, it also influences the precipitation–dissolution reactions, redox reactions, mobility, leaching and dispersion of colloids [19,68,88,89]. While soil pH is the most important or master variable that drives metal availability in soil-plant systems, other factors such as CEC and Eh may also affect solubility, mobility, and bioavailability. Bravo et al. [88] suggest that reducing conditions marked by a significant drop in the Eh and low pH lead to the formation of metal sulfides, but these are quite insoluble such that metal mobility and bioavailability are considerably less than would be expected in oxidized soils. As such, the oxidation state and chemical species influence the reactivity and mobility of metals in the environment.

In addition, other physicochemical properties of elements including electronegativity and ionic potential affect the phytogeochemical behavior of metals. For instance, electronegativity influences the order in which trace metals sorb on soil constituents [90]. Therefore, stronger covalent bonds with oxygen atoms form from highly electronegative metals. For some divalent metals, Kinraide et al. [91] suggest that the bonding preference based on electronenegativity is: Cu > Ni > Co > Pb > Cd > Zn > Mg > Sr. However, this pattern may differ on account of ionic potential (charge/radius ratio) which influences the bond strength and, thus, the preferential bonding would be Ni > Mg > Cu > Co > Zn > Cd > Sr > Pb [90,92]. In essence, chemical speciation plays a significant role in evaluating the metal's mobility, bioavailability and potential uptake by terrestrial plants. The effects of the different geochemical variables on the mobility and bioavailability of trace metals including Cu and Co are summarized in Table 2.

In addition to the effect of the highlighted geochemical variables on metal behavior in terrestrial plant systems, environmental, and landscape settings may also influence the mobility and bioavailability of trace metals. Cameron et al. [89] suggest that topography significantly affects the development of soil metal anomalies due to its influence on metal-rich groundwater flow from mineralized zones. This could be because the slope of the groundwater table and subsequent groundwater flow is usually a reflection of the surface gradient. However, proximal to drainage divides, groundwater flow may also be influenced by other factors including the fluctuation rate of the groundwater level in adjacent basins [1]. In low relief areas protracted by erosion such as the ZCB, this can lead to episodic movements of metal-rich groundwater unrelated to the immediate surface topography. Baseline soil geochemical surveys in the CACB suggest that anomalous metal concentrations in the freely drained soil horizons above the maximum level of the groundwater table are transported from deeper horizons by vegetation [1,93].

Bioavailability in plants is indicated by the readily soluble fraction of the metals even though there is a growing awareness that current methods of assessment of soluble and bioavailable fractions need reevaluation because of their variability over spatiotemporal scales [94]. Chemical extraction techniques remain the frequently used methods of estimating the fraction of a metal that is bioavailable. The soluble content of a metal and the "weakly adsorbed" content (i.e., exchangeable) provide a good measure of the plant-available amount [22,27]. Single extractants, including $CaCl_2$ and $Ca(NO_3)_2$, are frequently used to extract the exchangeable metals from the soil [27] and this exchangeable fraction may closely correlate with plant uptake.

Table 2. Effects of soil factors on trace metal mobility and bioavailability.

Soil Factor	Causal Process	Effect on Mobility/Bioavailability	Reference
Low pH	Decreasing sorption of cations onto oxides of Fe and Mn	Increase	[27,88]
	Increasing sorption of anions onto oxides of Fe and Mn	Decrease	[88]
High pH	Increasing precipitation of cations as carbonates and hydroxides	Decrease	[22,82]
	Increasing sorption of cations onto oxides of Fe and Mn	Decrease	[46,88]
	Increasing complexation of certain cations by dissolved ligands	Increase	[52]
	Increasing sorption of cations onto (solid) humus material	Decrease	[27,82,88]
	Decreasing sorption of anions	Increase	[52,71,72]
High clay content	Increasing ion exchange for trace cations (at all pH)	Decrease	[52,72]
High OM (solid)	Increasing sorption of cations onto humus material	Decrease	[88]
Competing ions	Increasing competition for sorption sites	Increase	[91]
Dissolved inorganic ligands	Increasing trace metal solubility	Increase	[95]
Dissolved organic ligands	Increasing trace metal solubility	Increase	[96]
Fe and Mn oxides	Increasing sorption of trace cations with increasing pH	Decrease	[97]
	Increasing sorption of trace anions with decreasing pH	Decrease	[52,82,88]
Low redox	Decreasing solubility at low redox potential as metal sulfides	Decrease	[88,95]

Certain trace elements bioaccumulate more in plants when they are in aqueous media (e.g., Cu^{2+}, Ni^{2+}, Co^{2+} Ag^{+}) while others in alkylated form (e.g., methyl Hg).

3.5. Vegetation Geochemistry and Its Use as a Sampling Medium

Plants absorb and metabolize a wide range of elements from groundwater or mineral surfaces and accumulates or excludes others [98,99]. Biologically essential elements (P, Ca, K, Mg, Na, S, Cu, Fe, Mo, Se, and Zn) are selectively taken up by vegetation. Beneficial and non-essential elements including those that are potentially toxic are also taken up and may closely reflect the composition of the soil and regolith [14,100–102]. Cu is an essential plant micronutrient forming part of the protein structure for a range of enzymes that drive electron transport and redox reactions in plant organelles, including mitochondria, chloroplasts, cell walls and the cytoplasm of plant cells [83,103]. Cu-bearing proteins also play a critical role in carbohydrate and nitrogen metabolism as well as in the lignification of cell walls. Plants usually absorb Cu from the soil in the form of Cu^{2+} as this easily binds to organic matter compared to other copper species [86]. Since Cu is of nutritional value to plants, its content in most plants tends to be internally, rather than externally regulated. As such, most plants have Cu concentrations below those of the soil in which they grow (Table 3) with the exception of those that grow over mineralized areas [83]. The Cu concentration required for normal plant growth ranges from 5–20 mg·Kg^{-1} [95]. Deficiency and toxicity may be considered as concentrations below or above the provided range. However, upper thresholds suggesting significant bioaccumulation may vary across geological environments depending on the soil Cu concentrations. In mineralized areas, Cu concentrations in plants increases greatly over a small range of increasing concentrations in the soil to a point where the plant may not tolerate such harsh edaphic conditions [64,87]. Unlike Cu, plant Co concentrations tend to be strongly correlated to the soil chemistry because it is not normally regarded as an essential nutritional requirement, even though it may have beneficial effects [100,104].

Table 3. Mean elemental concentrations (mg·Kg^{-1}) in rocks, soils and vegetation: Source: Tooms and Webb [1].

	Co	Cr	Cu	Pb	Mn	Ni	Zn
Earth's crust	25	100	55	13	950	75	70
Granite	3	20	13	48	195	1	45
Basalt	47	114	110	8	1280	76	86
Ultramafic rocks	150	1600	10	1	1620	2000	50
Soils (non-ultramafic)	10	60	20	10	850	40	50
Soils (ultramafic)	250	2500	20	10	1000	2500	40
Vegetation (non-ultramafic)	1	1	10	10	80	2	100
Vegetation (ultramafic)	10	10	10	10	100	80	100

Floristic composition reflects the availability of elements in the roots and the ability of the plant to absorb, transport and accumulate elements. Plants tolerant to elevated metal concentrations respond by three mechanisms, namely; exclusion, indication, and hyperaccumulation [21,105]. Excluders restrict the transport of metals to the aboveground biomass and maintain relatively low folia metal concentrations over a wide range of metal concentrations in the soil. Indicator plant species tend to translocate and accumulate metals in the aboveground plant organs [96]. Metal concentration in these plants reflects the soil chemistry and plant to soil metal concentration ratio is relatively constant and demonstrates a linear relationship [28,106]. Hyperaccumulators display an extreme uptake of metals and translocation into the shoots [20,107]. The identification of excluder, indicator, and hyperaccumulator plants generally depends on the comparison of the metal concentration in the plant to the total metal concentration in the soil [24]. Indicator and hyperaccumulator plants have Cu concentrations in the range of 30–500 mg·Kg^{-1} [95], but this can vary depending on the underlying rock units and soil composition.

Metal uptake by vegetation may be element, plant species and plant tissue specific [4,28]. Metal concentrations in plants usually show variation amongst plant species [14,107]. The concentration, transfer, and accumulation of metals from the soil to the roots and shoots are evaluated based on biological concentration factors (BCF). Bioconcentration factor (BCF) is calculated as the ratio of metal content in plant roots to soil and has been a useful measure of phytoremediation potential [108]. As such, metal uptake is constrained from the bioconcentration factors of sampled plant species using Equation (1).

$$\text{Bioconcentration Factor(BCF)} = {C_{metal\ in\ plant}}\Big/{C_{metal\ in\ soil}} \quad (1)$$

The bioconcentration factors of metals are indices that are used to determine the plant species' ability to concentrate the metals of interest with respect to the soils and underlying mineralized rocks. Plant species with BCF > 1 may be accumulators or hyperaccumulator plants and may indicate potential for mineralization. However, in mineral exploration campaigns, systematic soil, and vegetation sampling remains important to determine whether the high bioconcentration factors are due to natural metal enrichment or simply a consequence of anthropogenic activities.

Vegetation sampling has gained traction as an exploration approach in the northern hemisphere and parts of the tropics [5,10,23,25,96]. For instance, Lottermoter et al. [23] evaluated the biogeochemistry of three Pb–Zn gossans in northwest Australia and results suggest moderate ($R > 0.5$) to strong positive correlation ($R > 0.9$) between Pb and the gossan colonizing plant species namely; *Sida* sp., *Paraneurachne muelleri*, *Sena costata*, *Acacia lysiphloia* and *Troidia molesta*. Zn showed strong positive correlation with the species *Sida* sp., *Cleome viscosa* and *T. molesta*. In the Ghanzi area of Botswana, Cole et al. [109] used *Helichrysum leptolepis* to indicate Cu mineralized rocks in areas affected by shallow weathering. Deeper rooting shrubs, *Ecbolium lugardiae* were also used to locate Cu mineralization obscured by a thick blanket of sand in Ngwako Pan area, Ngamiland. In addition, Nkoane et al. [25] carried out phytogeochemical exploration at three Cu–Ni mineralized sites in Botswana and identified *Helischrysum candolleaunum* and *Blepharis diverspinia* as candidate species indicative of mineralized zones. The species, *H. candolleanum* demonstrates hyperaccumulation with aboveground biomass concentrations of 20–2000 mg/Kg Cu and 6–210 mg/Kg Ni.

In the Central African Copperbelt, several Cu and Co indicator species have been identified from ecological restoration studies [13,22,102,110]. Despite the reported metal uptake and speciation in plants, the independent geological and phytogeochemistry variables that underpin the relationship between plant species and mineralized areas have not been fully described. This offers an opportunity for the deployment of phytogeochemistry as a potential method for the search and discovery of ore deposits.

Plant–Soil Sampling and Analyses

Phytogeochemistry in mineral exploration depends on the plant–soil correlation. This is because plants are not able to access the total metal pool available in the soil. Thus, an assessment of the geochemical forms of Cu and Co in the rhizosphere and an evaluation of their effect on metal bioavailabilty requires systematic plant and soil sampling [21,87,111]. Metal phytoavailability is highly plant specific and relies on soil properties that control the mobility and bioavailability of metals in the soil solution phases [94,108]. Cu and Co have a strong affinity for soils with clay and organic constituents as these tend to decrease element mobility [19,112]. Cu in soil solution phases can also occur in association with other ligands such as NH_3, $H_2PO_4{}^{2-}$, $SO_4{}^{2-}$, OH^-, Cl^- [52]. The speciation of metals in soils also depends on soil pH. Changes in metal speciation are considered as a fundamental indicator of variation in metal mobility and bioavialability in soil-plant systems [83].

Thus, in phytogeochemical exploration, both plant and soil samples are systematically collected using a regular grid. The approach taken in vegetation sampling is the quadrat quantitative ecological technique [3] in which different sizes of quadrats including 100 m^2, 25 m^2, and 1 m^2, are taken for trees, shrubs, and herbaceous vegetation, respectively. Different organs of the plants including roots, stems and leaves are collected from each of the sampled species. Soils are sampled using the traditional soil geochemical sampling targeting the B-horizon [1]. In addition, Alekseenko et al. [113] suggest sampling soils dislodged from plant roots to determine the potential metal enrichment relative to the background concentrations in the soil.

Field samples are usually analyzed for various physicochemical properties including soil electrical conductivity (EC), pH, total dissolved solids (TDS) and textural characteristics, i.e., whether the soil is sandy, silty, or clay soil [22,114]. Both plant and soil samples are homogenized prior to chemical elemental analysis. Plants are ground to fine ash while soils are sieved to 76 microns as multi-element analyses of such reduced size fractions can reveal significant geological and geochemical processes [56]. Multi-element soil and plant elemental analysis is conducted using the pXRF [115]. This provides quick geochemical results even though certain trace elements, and some samples may have very low concentration below the limits of detection. However, current advances in analytical technologies, including the atomic absorption spectrometry (AAS), micro-PIXE (particle induced X-ray emission) spectroscopy, scanning electron microscopy with energy dispersive spectrometry (SEM-EDS), inductively coupled plasma-mass spectrometry (ICP-MS), Quemscan, and mineral laser ablation (MLA) present opportunities to conduct the elemental and mineral stoichiometry of the soil and plant samples [104,116,117]. These modern instruments can potentially address the analytical challenges associated with plant tissues that tend to accumulate very low concentrations of chemical elements. Furthermore, studies conducted on the herbarium material of *Haumaniastrum* specimens in the Central African Copperbelt using the SEM-EDS suggest the successful discrimination of Cu and Co species caused by surficial contamination in the internal plant structures [19,27,113]. However, these studies also recognize the lack of standard quality assurance and quality control protocols in vegetation sampling and the complexities in data analysis and interpretation arising from the collected samples.

4. Assessment Techniques for Use of Plant Species in Mineral Deposit Detection

The most effective approach towards assessing the use of plants in the search and discovery of concealed ore deposits depends on employing several assessment tools that can be grouped according to geochemical and metallophyte evaluation as shown in Figure 7. Geochemical evaluation in mineral exploration focuses on identifying chemical gradients that show spatial continuity and are related to alteration and mineralization processes [56]. An interpretation of geochemical data reveals large scale patterns that provide vectors to geological and geochemical processes that may have led to the preservation of an orebody, including zones of metal enrichment and depletion [59]. Effective and robust geochemical data interpretation typically reveals linear relationships which could represent the stoichiometry of rock forming minerals and subsequent processes that modify mineral structures, including hydrothermal alteration, weathering, and fluid-rock interactions [56,118].

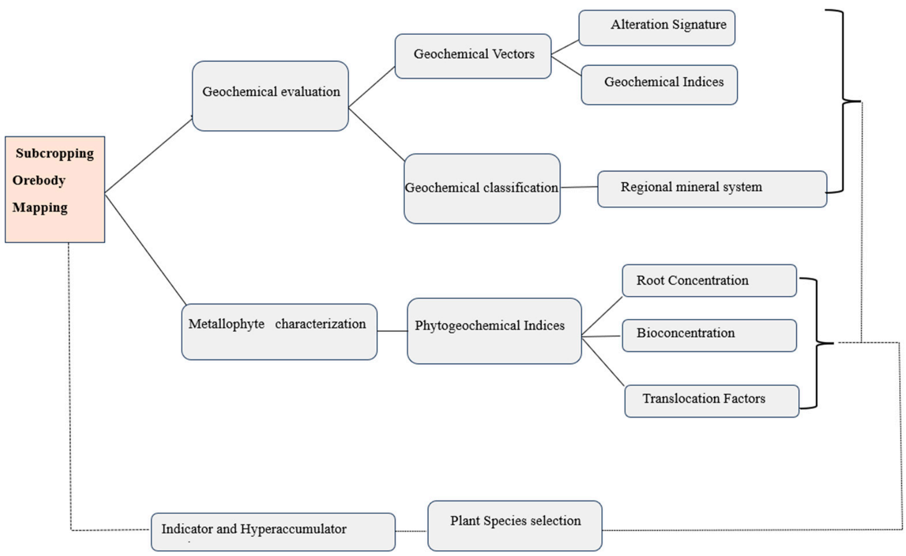

Figure 7. Conceptual framework of utilizing plants in mineral exploration.

However, regional to local scale geological and geochemical processes can also be revealed by geochemical indices. These indices are useful in distinguishing negative and non-significant anomalies from positive anomalies that are related to mineralized zones. For instance, scandium to copper (Sc/Cu) indices are used in normalizing geochemical data and validation of mapped anomalous targets [119]. In addition, ore deposit styles are characterized by unique clusters of elements and therefore, element associations revealed from geochemical indices may point to the metal sources and nature of mineralizing fluids [52,72]. In environmental geochemical surveys, geochemical indices include the geo-accumulation index (I_{geo}) and contamination factors (CFs) and these focus on elevated metal concentrations from anthropogenic sources [120].

However, metal enrichment in the soils and regolith affects plant species irrespective of whether it is from natural or anthropogenic sources. A plant's ability to accumulate metals from soils can be quantified using metal coefficients [25,95]. Metal transfer coefficients have been defined as the ratio of plant to soil metal concentrations. Such phytogeochemical indices allow an evaluation of the translocation of metals from the soils to plants. In Figure 7, three phytogeochemical indices that are relevant to metallophyte characterization have been given. The root concentration factor (RCF) is the ratio of metal concentration in the roots to the acid extractable metal concentration in the soil. A plant's ability to translocate metals from the roots to the foliage is measured using the translocation factor (TF) which is the ratio of metal concentration in the foliage to that in the roots. Plants that absorb and accumulate metals tend to have high RCF and TF values. Metallophytes with high RCF and TF values are useful in mineral exploration. Such plants are suitable for mineral exploration because they accumulate and translocate metals from mineralized zones into their roots and, subsequently, to their aboveground biomass. Selection of these accumulator and hyperaccumulator species is essential in mineral exploration and may be achieved by linking geochemical drivers to the resultant phytogeochemical indices.

4.1. Metallophytes in the Central African Copperbelt

Cu–Co metallophytes were first described from the CACB in the 1930s and extensive research into these higher plants took place from the 1950–60s [1] during which significant ore deposits were discovered. However, geobotanical and phytogeochemical exploration did not progress beyond the 1970s in the CACB probably due to the easily mappable outcropping mineralized rocks. Despite this limited growth in the knowledge of the application of phytogeochemistry in mineral exploration, there have been several recent studies in the CACB focused on the assessment of heavy metal accumulation for environmental restoration [21,28,121]. Such studies suggest additional potential for mineral prospecting.

Several plant species that demonstrate Cu and Co tolerance have been identified in the CACB based on ecological restoration studies (Table 4). Among them are *Annona senegalensis*, *Aeolanthus biformifolius*, *Silene cobalticola*, *Ascolepis metallorum*, *Crotalaria cobalticola* and *Haumaniastrum*. The genus *Haumaniastrum* constitutes several species that usually grow on soils with elevated concentrations of Cu and Co, with one species (*H. robertii*) growing only over copper deposits in both Zambia and the DRC [21,66,122]. The species *Haumaniastrum robertii* was reported as a Cu–Co hyperaccumulator based on unwashed field folia samples with analytical results up to 8500 mg·Kg^{-1} Cu and 4000 mg·Kg^{-1} Co [19,122]. However, such elevated concentrations may also be attributed to windblown dust containing copper and cobalt from the metal rich soils. Another species of the genus *Haumaniastrum* that has shown hyperaccumulation properties is the *Haumaniastrum Katangese* which accumulates less Co (up to 864 mg·Kg^{-1}) but more Cu compared to *Haumaniastrum robertii*.

Table 4. Cu and Co hyperaccumulator plant species in the Central African Copperbelt (values in mg·Kg^{-1} dry mass).

Species	Cu	Co	Reference
Aeolanthus biformifolius	3920	2820	[27]
Annona senegalensis	2889	2650	[102]
Ascolepis metallorum	1200	-	[21]
Buchnera henriquessi	3520	2435	[106]
Bulbostylis mucronata	7783	2130	[13]
Becium homblei	2051	-	[105]
Crotalaria cobalticola	-	3010	[6]
Guternbergia cupricola	5095	2309	[107]
Haumaniastrum Katangese	8356	2240	[84]
Haumaniastrum robertii	8500	4000	[122]
Haumaniastrum rosulatum	1089	-	[19]
Ipomoea alpina	12,300	-	[27]
Lupinus perennis	9322	2300	[101]
Rendlia cupricola	1560	-	[65]
Parinari curatellifolia			[102]

Experimental work has supplemented some of the field ecological studies in which two-month-old plants collected from seeds were exposed to soluble Cu and Co salts mixed with soil and used in simulating natural conditions [27]. The results of these experiments suggest that *H. robertii* may be tolerant to soil Cu and Co concentrations of up to 8500 $mg \cdot Kg^{-1}$ and 4000 $mg \cdot Kg^{-1}$, respectively [19]. Other cuprophytes known to grow almost exclusively on metal rich soils with elevated concentrations of Cu include the species *Becium metallorum* (Duvign), *Becium Homblei* (de Wild), and various species of *Icomum* [106]. However, the species *H. robertii, H. Katangese* and *Becium Homblei* are probably the best-known Cu–Co indicator plant species [64,123]. Field ecological investigations into the species, *Becium Homblei* suggests that it can be tolerant to soil Cu and Ni concentrations of up to 15,000 $mg \cdot Kg^{-1}$ and 5000 $mg \cdot Kg^{-1}$ respectively [124]. Consequently, *Becium Homblei*, a member of the Labiatae (mint family) is commonly used as a geobotanical indicator by geologists in Zambia [1] even though its phytogeochemical significance remains unclear.

While *Becium Homblei* has been associated with elevated soil Cu concentrations and stunted vegetation, commonly referred to as "copper clearings" in Zambia [1,124,125], geochemical exploration campaigns have not targeted sampling and analysis of these plant species. In addition, Matakala et al. [102] highlight *Annona senegalensis*, *Parinari curatellifolia* and *Dombeya rotundilifolia* as the native tree species in the ZCB with the ability to accumulate Cu and Co in their shoot tissues. Nonetheless, to employ phytogeochemistry in mineral exploration, there should be a clear geochemical footprint in the plants representing ore forming processes and possible orebody preservation [5] but information of such relationships that would be useful in phytogeochemistry application is currently limited.

4.2. Phytogeochemistry Integrative Exploration Approaches

Current advances in remote sensing and machine learning methods suggest promising opportunities for the integration of phytogeochemistry in regional and local scale mineral exploration. Chakraborty et al. [6] highlight that local to regional scale hyperspectral data can detect spectral changes in vegetation that may indicate the presence of an ore deposit and its pathfinder elements. Hyperspectral remote sensing measures radiated, emitted, and absorbed energy at hundreds of narrow and spectrally adjacent wavelengths. Hyperspectral remote sensing can span over various optical domains such as the visible (VIS; 400–700 nm), near infrared (NIR; 700–1200 nm), shortwave infrared (SWIR; 1000–2500 nm), midwave infrared (MWIR; 3000–7000 nm) and longwave infrared (LWIR; 7000–13,000 nm) [126–128]. The VIS–SWIR regions of the electromagnetic spectrum enable the detection and identification of hydrated minerals [129,130]. Vegetation typically demonstrates a spectral response through a combination of morphological parameters, such as canopy structure, leaf area, and chemical properties, such as water content, chlorophyll, nitrogen, and trace metals concentration [6,129,131]. According to Rathod et al. [132], trace elements, even at low concentrations, can still cause subtle changes in the spectral signature of vegetation across the VIS and SWIR regions of the electromagnetic spectrum. Remote sensing provides a cost-effective and efficient exploration approach allowing for a thorough spatial coverage of the Earth's surface, however, its integration with phytogeochemistry requires additional environmental variables including soil types, topography, biotic, and abiotic interactions. In addition, sensitivity studies derived from remote sensing should be considered to understand the downside and effects of different data collection and processing methods [133,134].

Emerging technologies like machine learning (ML) and deep learning (DL) are increasingly gaining remarkable attention and revolutionizing multi-source data integration in various fields including the earth sciences [58,60,61,135–137]. ML methods have attained outstanding results in the regression estimation of bio-geo-physical parameters from remotely sensed reflectance at local and global scales [138,139]. These approaches emphasize spatial prediction and could be relevant in the integration and application of phytogeochemistry in mineral exploration. Several machine learning algorithms including K-Nearest neighbor (KNN), linear regression (LR), random forest (RF), least absolute shrinkage, and selection operator (LASSO), support vector machines (SVM), support vector regression (SVR), and decision tree (DT) have been used in modeling phytoremediation and prediction of heavy metal bioaccumulation in soil–plant systems [140–142]. In terms of geochemical modeling, most studies have focused on the simulation of metal accumulation in soils or water bodies in conjunction with geographic information and metal adsorption behavior based on data extracted from literature [140,143,144]. ML techniques have demonstrated robust prediction accuracy and could be useful in integrating phytogeochemical data for mineral exploration. For instance, Xu et al. [145] used an ensemble model by optimized SVM (R^2 = 0.88) to estimate Zn concentration in polluted soils of Shandong province in China. In addition, deep learning methods extend the envelope of knowledge by using artificial neural networks (ANN), convolutional neural networks (CNN), and convolutional long short-term memory (Conv LSTM) in extracting deep features from complex multi-source datasets through multiple kernel learning [146,147] and therefore, provide improved accuracy and prediction capabilities. Bazoobandi et al. [148] improved the R^2 of soil Cd and Pb content prediction from 0.47 obtained by multiple linear regression (MLR) to 0.83 using ANN and identified soil organic carbon (SOC) as the most significant factor.

Despite the advantages of ML and DL, several challenges still need to be addressed to attain the best performance and predictive power of the models, including insufficient or inappropriate training data samples, data discrepancies due to different experimental methods, and improper selection of input variables [136]. Insufficient feature inputs may lead to low prediction accuracy and miss important factors that are relevant to accurate model prediction. Therefore, when employing ML and DL algorithms to spatially predict metal accumulation in plants related to ore deposits, all the variables influencing metal accumulation in plants must be considered.

5. Challenges and Opportunities for the Application of Phytogeochemistry

Despite the bottlenecks in the deployment of phytogeochemistry in mineral exploration campaigns in the CACB, several opportunities provide enough room for developing plant species sampling to define geochemical exploration targets in the region. We highlight some of the existing challenges and opportunities for developing site specific and candidate species targeted for phytogeochemical exploration in the Central African Copperbelt.

5.1. Challenges

Based on the literature review, we enumerate the inherent challenges associated with the use of geochemical plant species sampling in mineral exploration and these should be with consideration of site-specific conditions. The main challenges include:

(1) The lack of statistical and spatial relationships between indicator and pathfinder elements in terrains where geochemical plant species sampling has been conducted as most studies characterize metal accumulation in plants based on uni-element concentrations, rather than considering a multi-element approach. However, an ideal plant useful as an indicator species in mineral exploration should be able to tolerate and accumulate a range of metals since secondary geochemical expressions of mineral systems including sediment-hosted Cu–Co deposits tend to exhibit unique clusters of element associations. Currently there are no plants known in the CACB that meet these criteria.

(2) Metal species in terrestrial plant ecosystems are affected by complex interactions between plant roots and soil microbial communities in the rhizosphere. These interactions and their impact on Cu–Co availability in plants is currently poorly understood in the CACB and thus, requires cutting edge research implementing advanced methods. However, certain mining regions including developing countries such as Zambia and DRC may suffer from limited resources and infrastructure which hinders the collection of adequate data, processing and sharing of reproducible research results.

(3) The limited multi-disciplinary research among expert geoscientists, geochemists, and plant taxonomists affects the quality of phytogeochemical data. The challenge lies

in differentiating between natural accumulation and contamination as well as the accurate identification of plant species since several species may exist over a single exploration site. As such, it becomes challenging to define a geochemical contrast related to an ore deposit.

(4) The lack of definite quality assurance and quality control protocols, including the use of standards, blanks, and duplicates, is another major challenge associated with the use of the geochemistry of terrestrial plants in mineral exploration as most studies do not explicitly state how the phytogeochemical data was checked for precision and accuracy. Additionally, the ability of certain plants to grow on both mineralized and non-mineralized areas make it difficult to precisely select duplicates and blanks during a phytogeochemical exploration program and thus, affecting the reliability of phytogeochemical datasets.

(5) Phytogeochemistry cannot be executed independently, as metal accumulation in plants is always affected by soil properties including the solubility and bioavailability of metals for uptake by plants from the soil. In addition, several factors should be considered when sampling vegetation. These include plant species distribution and suitability of the root structure [21], variation in elemental concentrations in different plant organs [113,123], and the age and health of the plant being sampled. Another considerable factor is the influence of seasonality on chemical structures, especially the water uptake of plants which may dilute certain elements in wet season and concentrate them during the dry season [149].

(6) The mineralogy of the underlying rocks may affect the biovailability of Cu–Co for uptake by terrestrial plants since clay rich rocks such as shales and siltstones have higher metal retention capacities compared to quartzo-feldspathic and carbonate rocks. This may result in very low trace element concentrations in plants and thus, requires advanced analytical technologies for detection of geochemical signatures in plants that warrant mineral exploration efforts.

5.2. Opportunities

Regardless of the highlighted challenges, several opportunities are available to enable the deployment and integration of plant species sampling in geochemical exploration campaigns in the CACB. These opportunities include:

(1) The high diversity of plant communities and species richness of the CACB owing to its complex and varied geological setting. This plant diversity and richness could be leveraged in selecting candidate species demonstrating tolerance and accumulation of a range of elements in their below and/or aboveground biomass at geochemical anomalous concentrations.

(2) The recognition of plants colonizing mineralised sites and mining generated wastelands in the CACB including their analysis for Cu–Co accumulation presents baseline data and thus, phytogeochemistry could leverage on such species in simulating geochemical patterns from brownfield or known mineralized sites to greenfield areas that have not been affected by mining.

(3) The successful application of hyperaccumulators for phytoremediation [3,14] presents opportunities for employing multi-element phytogeochemistry in the selection of indicator plant species as vectors to mineralized zones.

(4) Current advances in multivariate biogeochemical data analysis [10] and the deployment of data driven approaches, such as machine learning and deep learning algorithms, for predictive mapping and indicator species selection [150] provide a basis for enhancing the potential of phytogeochemistry in mineral exploration.

(5) Collaborative research within the CACB and with international research institutions and cooperative partners will address the limited access to advanced analytical tools, expertise and research funding. Such collaborations will enable the adoption of modern data driven approaches and make available the costly superfast computers with high computational power capable of crunching big data and managing ML and

DL models. Utilization of multi-disciplinary research integrating biological, chemical, and geological information should enable the wider application of phytogeochemistry in mineral exploration.

6. Conclusions and Future Directions

The diverse geological setting of the CACB suggests a varied litho- and soil-geochemistry which ultimately impacts on the region's floristic composition. This presents a wide pool for selection of suitable site-specific plant species that have specific response patterns towards particular mineralization styles and accumulate a range of trace elements. Despite the release of several trace elements and metal ions during the weathering of Katangan rocks, their speciation in soil-plant systems is driven by several geochemical processes including ion exchange (adsorption-desorption), solubilization and absorption. These processes are influenced by various geochemical factors including pH, Eh, organic matter, cation exchange capacity, and oxides of Fe, Mn and Al. These geochemical factors play a major role in controlling trace element mobility, bioavailability and uptake in soil-plant systems. In addition, other physicochemical properties of elements such as electronegativity and ionic potential affect the phytogeochemical behavior of metals. The concentration, translocation, and accumulation of trace elements from the soil to plant organs is quantified using the biological concentration factors and plant species with BCF > 1 are hyperaccumulators and have been inferred as potential candidate species for phytogeochemical exploration of ore deposits. In addition, the implementation of terrestrial plant species sampling for ore deposit discoveries in the tropical regions suggests a great promise for sediment hosted Cu–Co exploration in the CACB.

However, phytogeochemistry requires an integrated mineral exploration approach in its deployment due to the complex biotic and abiotic interactions in terrestrial plant ecosystems. Emerging mineral exploration technologies, such as hyperspectral remote sensing, machine learning, and deep learning techniques, offer several opportunities for the integration of phytogeochemistry in mineral exploration. These approaches offer potential benefits in terms of multi-source data integration, accuracy and speed in predictive mapping of ore deposits.

As the cost of conducting mineral exploration increases and discovery success rates decrease, there is an urgent need to develop new effective and low-cost exploration methods. Phytogeochemistry is one such potential method. In addition, there is rising global interest for low impact and eco-friendly exploration technologies which highlight plant species sampling as a potential target generation criteria. To evaluate its utility will require additional research in terms of identifying target species and defining rigorous sampling techniques. Targeted multi-disciplinary research projects focused on these species and integrating multi-source data are required to evaluate the true promise of phytogeochemistry.

Chemical analyses of metallophyte species in the CACB indicate their suitability for phytoremediation of degraded landscapes and therefore, could be useful in mineral exploration targeting although these analyses are limited to analysis for Cu and Co. As such, phytogeochemical exploration needs to move towards multi-element and stable isotopic analyses of plant tissues in order to fingerprint mineralization over spatiotemporal scales. Such phytogeochemical datasets will enable the linkages among geological and geochemical variables in mineralized systems and stable isotopes can also act as tracers of observed metal concentrations in plant media. In addition, analyses of chemical constituents of tree rings may prove useful in providing spatiotemporal geochemical data and these datasets can benchmark regional and local geochemical thresholds and address anthropogenic inputs from background sources during phytogeochemical data interpretation in mineral exploration. Additionally, there is lack of consistency regarding the type(s) of plant organs to be sampled during phytogeochemical exploration as some studies have sampled roots, stems and leaves while other studies have only sampled foliage. Therefore, there is need to define sampling guidelines for effective implementation of phytogeochemistry in mineral exploration.

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References

1. Tooms, J.S.; Webb, J.S. Geochemical Prospecting Investigations in the Northern Rhodesian Copperbelt. *Econ. Geol.* **1961**, *56*, 815–846. [CrossRef]
2. Fleischer, V.D. Discovery, Geology and Genesis of Copper—Cobalt Mineralisation at Chambishi Southeast Prospect, Zambia. *Precambrian Res.* **1984**, *25*, 119–133. [CrossRef]
3. Rahman, I.U.; Afzal, A.; Iqbal, Z.; Bussmann, R.W.; Alsamadany, H.; Calixto, E.S.; Shah, G.M.; Kausar, R.; Shah, M.; Ali, N.; et al. Ecological Gradients Hosting Plant Communities in Himalayan Subalpine Pastures: Application of Multivariate Approaches to Identify Indicator Species. *Ecol. Inform.* **2020**, *60*, 101162. [CrossRef]
4. Sun, Z.; Chen, J.; Wang, X.; Lv, C. Heavy Metal Accumulation in Native Plants at a Metallurgy Waste Site in Rural Areas of Northern China. *Ecol. Eng.* **2016**, *86*, 60–68. [CrossRef]
5. Johnsen, A.R.; Thomsen, T.B.; Thaarup, S.M. Test of Vegetation-Based Surface Exploration for Detection of Arctic Mineralizations: The Deep Buried Kangerluarsuk Zn-Pb-Ag Anomaly. *J. Geochem. Explor.* **2021**, *220*, 106665. [CrossRef] [PubMed]
6. Chakraborty, R.; Kereszturi, G.; Pullanagari, R.; Durance, P.; Ashraf, S.; Anderson, C. Mineral Prospecting from Biogeochemical and Geological Information Using Hyperspectral Remote Sensing-Feasibility and Challenges. *J. Geochem. Explor.* **2022**, *232*, 106900. [CrossRef]
7. Dunn, C.E. New Perspectives on Biogeochemical Exploration. *Proc. Explor.* **2007**, *7*, 249–261.
8. Henne, A.; Reid, N.; Thorne, R.L.; Spinks, S.C.; Pinchand, T.; White, A. Multi-Media Geochemical Exploration in the Critical Zone: A Case Study over the Prairie and Wolf Zn–Pb Deposits, Capricorn Orogen, Western Australia. *Minerals* **2021**, *11*, 1174. [CrossRef]
9. Mou, N.; Wang, G.; Sun, X. Identification of Geochemical Anomalies Related to Mineralization: A Case Study from Porphyry Copper Deposits in the Qulong-Jiama Mining District of Tibet, China. *J. Geochem. Explor.* **2023**, *244*, 107126. [CrossRef]
10. Ghorbani, Z.; Gholizadeh, F.; Casali, J.; Hao, C.; Cavallin, H.E.; Van Loon, L.L.; Banerjee, N.R. Application of Multivariate Data Analysis to Biogeochemical Exploration at the Twin Lakes Deposit, Monument Bay Gold Project, Manitoba, Canada. *Chem. Geol.* **2022**, *593*, 120739. [CrossRef]
11. Wolff, K.; Hill, S.M.; Tiddy, C.; Giles, D.; Smernik, R.J. Biogeochemical Expression of Buried Iron-Oxide-copper-gold (IOCG) Mineral Systems in Mallee Eucalypts on the Yorke Peninsula, Southern Olympic Domain; South Australia. *J. Geochem. Explor.* **2018**, *185*, 139–152. [CrossRef]
12. Pratas, J.; Prasad, M.N.V.; Freitas, H.; Conde, L. Plants Growing in Abandoned Mines of Portugal Are Useful for Biogeochemical Exploration of Arsenic, Antimony, Tungsten and Mine Reclamation. *J. Geochem. Explor.* **2005**, *85*, 99–107. [CrossRef]
13. Sandell Festin, E.; Salk, C.; Tigabu, M.; Syampungani, S.; Christer Odén, P. Biological Traits of Tropical Trees Suitable for Restoration of Copper-Polluted Lands. *Ecol. Eng.* **2019**, *138*, 118–125. [CrossRef]
14. Asensio, V.; Flórido, F.G.; Ruiz, F.; Perlatti, F.; Otero, X.L.; Ferreira, T.O. Screening of Native Tropical Trees for Phytoremediation in Copper-Polluted Soils. *Int. J. Phytoremediation* **2018**, *20*, 1456–1463. [CrossRef]
15. Lei, K.; Pan, H.; Lin, C. A Landscape Approach towards Ecological Restoration and Sustainable Development of Mining Areas. *Ecol. Eng.* **2016**, *90*, 320–325. [CrossRef]
16. Khan, W.; Khan, S.M.; Ahmad, H.; Ahmad, Z.; Page, S. Vegetation Mapping and Multivariate Approach to Indicator Species of a Forest Ecosystem: A Case Study from the Thandiani Sub Forests Division (TsFD) in the Western Himalayas. *Ecol. Indic.* **2016**, *71*, 336–351. [CrossRef]
17. Moher, D.; Liberati, A.; Tetzlaff, J.; Altman, D.G. Preferred Reporting Items for Systematic Reviews and Meta-Analyses: The PRISMA Statement. *Int. J. Surg.* **2010**, *8*, 336–341. [CrossRef]
18. Gurevitch, J.; Koricheva, J.; Nakagawa, S.; Stewart, G. Meta-Analysis and the Science of Research Synthesis. *Nature* **2018**, *555*, 175–182. [CrossRef] [PubMed]

19. Lange, B.; Pourret, O.; Meerts, P.; Jitaru, P.; Cancès, B.; Grison, C.; Faucon, M.P. Copper and Cobalt Mobility in Soil and Accumulation in a Metallophyte as Influenced by Experimental Manipulation of Soil Chemical Factors. *Chemosphere* **2016**, *146*, 75–84. [CrossRef]
20. Pollard, A.J.; Reeves, R.D.; Baker, A.J.M. Facultative Hyperaccumulation of Heavy Metals and Metalloids. *Plant Sci.* **2014**, *217–218*, 8–17. [CrossRef] [PubMed]
21. Ilunga wa Ilunga, E.; Mahy, G.; Piqueray, J.; Séleck, M.; Shutcha, M.N.; Meerts, P.; Faucon, M.P. Plant Functional Traits as a Promising Tool for the Ecological Restoration of Degraded Tropical Metal-Rich Habitats and Revegetation of Metal-Rich Bare Soils: A Case Study in Copper Vegetation of Katanga, DRC. *Ecol. Eng.* **2015**, *82*, 214–221. [CrossRef]
22. Perlatti, F.; Ferreira, T.O.; Romero, R.E.; Costa, M.C.G.; Otero, X.L. Copper Accumulation and Changes in Soil Physical–Chemical Properties Promoted by Native Plants in an Abandoned Mine Site in Northeastern Brazil: Implications for Restoration of Mine Sites. *Ecol. Eng.* **2015**, *82*, 103–111. [CrossRef]
23. Lottermoser, B.G.; Ashley, P.M.; Munksgaard, N.C. Biogeochemistry of Pb-Zn Gossans, Northwest Queensland, Australia: Implications for Mineral Exploration and Mine Site Rehabilitation. *Appl. Geochem.* **2008**, *23*, 723–742. [CrossRef]
24. Lintern, M.J.; Butt, C.R.M.; Scott, K.M. Gold in Vegetation and Soil—Three Case Studies from the Goldfields of Southern Western Australia. *J. Geochem. Explor.* **1997**, *58*, 1–14. [CrossRef]
25. Nkoane, B.B.M.; Sawula, G.M.; Wibetoe, G.; Lund, W. Identification of Cu and Ni Indicator Plants from Mineralised Locations in Botswana. *J. Geochem. Explor.* **2005**, *86*, 130–142. [CrossRef]
26. Cailteux, J.L.H.; Kampunzu, A.B.; Lerouge, C.; Kaputo, A.K.; Milesi, J.P. Genesis of Sediment-Hosted Stratiform Copper–Cobalt Deposits, Central African Copperbelt. *J. Afr. Earth Sci.* **2005**, *42*, 134–158. [CrossRef]
27. Lombi, E.; Scheckel, K.G.; Kempson, I.M. In Situ Analysis of Metal(Loid)s in Plants: State of the Art and Artefacts. *Environ. Exp. Bot.* **2011**, *72*, 3–17. [CrossRef]
28. Lange, B.; van der Ent, A.; Baker, A.J.M.; Echevarria, G.; Mahy, G.; Malaisse, F.; Meerts, P.; Pourret, O.; Verbruggen, N.; Faucon, M.P. Copper and Cobalt Accumulation in Plants: A Critical Assessment of the Current State of Knowledge. *New Phytol.* **2017**, *213*, 537–551. [CrossRef] [PubMed]
29. Eerola. T New Low-Impact Mineral Exploration Technologies and the Social License to Explore: Insights from Corporate Websites in Finland. *Clean. Environ. Syst.* **2021**, *3*, 100059. [CrossRef]
30. Prince, J.K.G.; Rainbird, R.H.; Wing, B.A. Evaporite Deposition in the Mid-Neoproterozoic as a Driver for Changes in Seawater Chemistry and the Biogeochemical Cycle of Sulfur. *Geology* **2019**, *47*, 375–379. [CrossRef]
31. Och, L.M.; Shields-Zhou, G.A. The Neoproterozoic Oxygenation Event: Environmental Perturbations and Biogeochemical Cycling. *Earth Sci. Rev.* **2012**, *110*, 26–57. [CrossRef]
32. Zientek, M.L.; Hammarstrom, J.M.; Johnson, K.M.; Bliss, J.D.; Broughton, D.W.; Christie, M.; Denning, P.D.; Hayes, T.S.; Hitzman, M.W.; Horton, J.D.; et al. *Global Mineral Resource Assessment Sediment-Hosted Stratabound Copper Assessment of the Neoproterozoic Roan Group, Central African Copperbelt, Katanga Basin, Democratic Republic of the Congo and Zambia*; US Geological Survey: Reston, VI, USA, 2014. [CrossRef]
33. Taylor, C.D.; Douglas Causey, J.; Denning, P.D.; Hammarstrom, J.M.; Hayes, T.S.; Horton, J.D.; Kirschbaum, M.J.; Parks, H.L.; Wilson, A.B.; Wintzer, N.E.; et al. *Scientific Investigations Report 2010-5090-J Global Mineral Resource Assessment Descriptive Models, Grade-Tonnage Relations, and Databases for the Assessment of Sediment-Hosted Copper Deposits-With Emphasis on Deposits in the Central African Copperbelt, Democratic Republic of the Congo and Zambia*; U.S. Geological Survey: Reston, VA, USA, 2013.
34. SEG. SEG Newsletter 81. *SEG Discov.* **2010**, *81*, 1–56. [CrossRef]
35. Singer, D.A. Future Copper Resources. *Ore Geol. Rev.* **2017**, *86*, 271–279. [CrossRef]
36. Hitzman, M.W.; Selley, D.; Bull, S. Formation of Sedimentary Rock-Hosted Stratiform Copper Deposits through Earth History. *Econ. Geol.* **2010**, *105*, 625–639. [CrossRef]
37. Kipata, M.L.; Delvaux, D.; Sebagenzi, M.N.; Cailteux, J.; Sintubin, M. Brittle Tectonic and Stress Field Evolution in the Pan-African Lufilian Arc and Its Foreland (Katanga, DRC): From Orogenic Compression to Extensional Collapse, Transpressional Inversion and Transition to Rifting. *Geol. Belg.* **2013**, *16*, 1–17.
38. Twite, F.; Broughton, D.; Nex, P.; Kinnaird, J.; Gilchrist, G.; Edwards, D. Lithostratigraphic and Structural Controls on Sulphide Mineralisation at the Kamoa Copper Deposit, Democratic Republic of Congo. *J. Afr. Earth Sci.* **2019**, *151*, 212–224. [CrossRef]
39. Frimmel, H.E.; Miller, R.M.G. Chapter 5.2 Continental Rifting. *Dev. Precambrian Geol.* **2009**, *16*, 153–159. [CrossRef]
40. Cailteux, J.L.H.; De Putter, T. The Neoproterozoic Katanga Supergroup (D. R. Congo): State-of-the-Art and Revisions of the Lithostratigraphy, Sedimentary Basin and Geodynamic Evolution. *J. Afr. Earth Sci.* **2019**, *150*, 522–531. [CrossRef]
41. Hitzman, M.W. Source Basins for Sediment-Hosted Stratiform Cu Deposits: Implications for the Structure of the Zambian Copperbelt. *J. Afr. Earth Sci.* **2000**, *30*, 855–863. [CrossRef]
42. Dewaele, S.; Muchez, P.; Vets, J.; Fernandez-Alonzo, M.; Tack, L. Multiphase Origin of the Cu-Co Ore Deposits in the Western Part of the Lufilian Fold-and-Thrust Belt, Katanga (Democratic Republic of Congo). *J. Afr. Earth Sci.* **2006**, *46*, 455–469. [CrossRef]
43. Batumike, M.J.; Cailteux, J.L.H.; Kampunzu, A.B. Lithostratigraphy, Basin Development, Base Metal Deposits, and Regional Correlations of the Neoproterozoic Nguba and Kundelungu Rock Successions, Central African Copperbelt. *Gondwana Res.* **2007**, *11*, 432–447. [CrossRef]

44. Mambwe, P.; Delpomdor, F.; Lavoie, S.; Mukonki, P.; Batumike, J.; Muchez, P. Sedimentary Evolution and Stratigraphy of the ~765–740 Ma Kansuki-Mwashya Platform Succession in the Tenke-Fungurume Mining District, Democratic Republic of the Congo. *Geol. Belg.* **2020**, *23*, 69–85. [CrossRef]
45. Mambwe, P.; Swennen, R.; Cailteux, J.; Mumba, C.; Dewaele, S.; Muchez, P. Review of the Origin of Breccias and Their Resource Potential in the Central Africa Copperbelt. *Ore Geol. Rev.* **2023**, *156*, 105389. [CrossRef]
46. Muchez, P.; Corbella, M. Factors Controlling the Precipitation of Copper and Cobalt Minerals in Sediment-Hosted Ore Deposits: Advances and Restrictions. *J. Geochem. Explor.* **2012**, *118*, 38–46. [CrossRef]
47. Mambwe, P.; Milan, L.; Batumike, J.; Lavoie, S.; Jébrak, M.; Kipata, L.; Chabu, M.; Mulongo, S.; Lubala, T.; Delvaux, D.; et al. Lithology, Petrography and Cu Occurrence of the Neoproterozoic Glacial Mwale Formation at the Shanika Syncline (Tenke Fungurume, Congo Copperbelt; Democratic Republic of Congo). *J. Afr. Earth Sci.* **2017**, *129*, 898–909. [CrossRef]
48. Williams, P.R.; Nisbet, B.W. Structural Framework of the Lufilian Fold Belt in the Domes Region of North Western Province, Zambia from Interpretation of Geophysical Data. *J. Afr. Earth Sci.* **2017**, *129*, 542–557. [CrossRef]
49. Halley, S.; Wood, D.; Stoltze, A.; Godfroid, J.; Goswell, H.; Jack, D. SEG-Newsletter-104-2016-January-Articleonly. *Soc. Econ. Geol.* **2016**, *104*, 1–21.
50. Muchez, P.; Brems, D.; Clara, E.; De Cleyn, A.; Lammens, L.; Boyce, A.; De Muynck, D.; Mukumba, W.; Sikazwe, O. Evolution of Cu–Co Mineralizing Fluids at Nkana Mine, Central African Copperbelt, Zambia. *J. Afr. Earth Sci.* **2010**, *58*, 457–474. [CrossRef]
51. Koegelenberg, C.; Basson, I.J.; Sinkala, H.; Lupapulo, H.; Hornsby, P. Pan-African Structural Evolution of Paleoproterozoic Basement Gneiss and Cu-Co Mineralized Shear Zones in the Domes Region of the Lufilian Belt, Mwombezhi Dome, Zambia. *J. Struct. Geol.* **2019**, *127*, 103869. [CrossRef]
52. Fontaine, L.; De Putter, T.; Bernard, A.; Decrée, S.; Cailteux, J.; Wouters, J.; Yans, J. Complex Mineralogical-Geochemical Sequences and Weathering Events in the Supergene Ore of the Cu–Co Luiswishi Deposit (Katanga, D.R. Congo). *J. Afr. Earth Sci.* **2020**, *161*, 103674. [CrossRef]
53. Kampunzu, A.B.; Cailteux, J.L.H.; Moine, B.; Loris, H.N.B.T. Geochemical Characterisation, Provenance, Source and Depositional Environment of 'Roches Argilo-Talqueuses' (RAT) and Mines Subgroups Sedimentary Rocks in the Neoproterozoic Katangan Belt (Congo): Lithostratigraphic Implications. *J. Afr. Earth Sci.* **2005**, *42*, 119–133. [CrossRef]
54. Large, R.R.; Bull, S.W.; McGoldrick, P.J. Lithogeochemical Halos and Geochemical Vectors to Stratiform Sediment Hosted Zn–Pb–Ag Deposits: Part 2. HYC Deposit, McArthur River, Northern Territory. *J. Geochem. Explor.* **2000**, *68*, 105–126. [CrossRef]
55. Sillitoe, R.H.; Perelló, J.; Creaser, R.A.; Wilton, J.; Dawborn, T. Two Ages of Copper Mineralization in the Mwombezhi Dome, Northwestern Zambia: Metallogenic Implications for the Central African Copperbelt. *Econ. Geol.* **2015**, *110*, 1917–1923. [CrossRef]
56. Grunsky, E.C.; Drew, L.J.; Sutphin, D.M. Process Recognition in Multi-Element Soil and Stream-Sediment Geochemical Data. *Appl. Geochem.* **2009**, *24*, 1602–1616. [CrossRef]
57. Hosseini-Dinani, H.; Aftabi, A. Vertical Lithogeochemical Halos and Zoning Vectors at Goushfil Zn–Pb Deposit, Irankuh District, Southwestern Isfahan, Iran: Implications for Concealed Ore Exploration and Genetic Models. *Ore Geol. Rev.* **2016**, *72*, 1004–1021. [CrossRef]
58. Kirkwood, C.; Cave, M.; Beamish, D.; Grebby, S.; Ferreira, A. A Machine Learning Approach to Geochemical Mapping. *J. Geochem. Explor.* **2016**, *167*, 49–61. [CrossRef]
59. Zuo, R.; Wang, J.; Yin, B. Visualization and Interpretation of Geochemical Exploration Data Using GIS and Machine Learning Methods. *Appl. Geochem.* **2021**, *134*, 105111. [CrossRef]
60. Sun, T.; Li, H.; Wu, K.; Chen, F.; Zhu, Z.; Hu, Z. Data-Driven Predictive Modelling of Mineral Prospectivity Using Machine Learning and Deep Learning Methods: A Case Study from Southern Jiangxi Province, China. *Minerals* **2020**, *10*, 102. [CrossRef]
61. Xiong, Z.; Cui, Y.; Liu, Z.; Zhao, Y.; Hu, M.; Hu, J. Evaluating Explorative Prediction Power of Machine Learning Algorithms for Materials Discovery Using K-Fold Forward Cross-Validation. *Comput. Mater. Sci.* **2020**, *171*, 109203. [CrossRef]
62. Sarafian, E.; Evans, R.L.; Abdelsalam, M.G.; Atekwana, E.; Elsenbeck, J.; Jones, A.G.; Chikambwe, E. Imaging Precambrian Lithospheric Structure in Zambia Using Electromagnetic Methods. *Gondwana Res.* **2018**, *54*, 38–49. [CrossRef]
63. Sono, P.; Nthaba, B.; Shemang, E.M.; Kgosidintsi, B.; Seane, T. An Integrated Use of Induced Polarization and Electrical Resistivity Imaging Methods to Delineate Zones of Potential Gold Mineralization in the Phitshane Molopo Area, Southeast Botswana. *J. Afr. Earth Sci.* **2021**, *174*, 104060. [CrossRef]
64. Boisson, S.; Monty, A.; Lebrun, J.; Séleck, M.; Mahy, G. Edaphic Niches of Metallophytes from Southeastern Democratic Republic of Congo: Implications for Post-Mining Restoration. *J. Nat. Conserv.* **2016**, *33*, 18–24. [CrossRef]
65. Faucon, M.-P.; Le Stradic, S.; Boisson, S.; Ilunga Wa Ilunga, E.; Séleck, M.; Lange, B.; Guillaume, D.; Shutcha, M.; Pourret, O.; Meerts, P.; et al. Agro-Bio Tech, 2 Passage Des Déportés. *Plant Soil.* **2016**, *5030*, 403–404.
66. Lange, B.; Delhaye, G.; Boisson, S.; Verbruggen, N.; Meerts, P.; Faucon, M.P. Variation in Copper and Cobalt Tolerance and Accumulation among Six Populations of the Facultative Metallophyte Anisopappus Chinensis (Asteraceae). *Environ. Exp. Bot.* **2018**, *153*, 1–9. [CrossRef]
67. Saad, L.; Parmentier, I.; Colinet, G.; Malaisse, F.; Faucon, M.P.; Meerts, P.; Mahy, G. Investigating the Vegetation-Soil Relationships on the Copper-Cobalt Rock Outcrops of Katanga (D. R. Congo), an Essential Step in a Biodiversity Conservation Plan. *Restor. Ecol.* **2012**, *20*, 405–415. [CrossRef]

68. Séleck, M.; Bizoux, J.P.; Colinet, G.; Faucon, M.P.; Guillaume, A.; Meerts, P.; Piqueray, J.; Mahy, G. Chemical Soil Factors Influencing Plant Assemblages along Copper-Cobalt Gradients: Implications for Conservation and Restoration. *Plant. Soil.* **2013**, *373*, 455–469. [CrossRef]
69. van der Ent, A.; Cardace, D.; Tibbett, M.; Echevarria, G. Ecological Implications of Pedogenesis and Geochemistry of Ultramafic Soils in Kinabalu Park (Malaysia). *Catena* **2018**, *160*, 154–169. [CrossRef]
70. Kříbek, B.; Majer, V.; Veselovský, F.; Nyambe, I. Discrimination of Lithogenic and Anthropogenic Sources of Metals and Sulphur in Soils of the Central-Northern Part of the Zambian Copperbelt Mining District: A Topsoil vs. Subsurface Soil Concept. *J. Geochem. Explor.* **2010**, *104*, 69–86. [CrossRef]
71. Ettler, V.; Mihaljevič, M.; Drahota, P.; Kříbek, B.; Nyambe, I.; Vaněk, A.; Penížek, V.; Sracek, O.; Natherová, V. Cobalt-Bearing Copper Slags from Luanshya (Zambian Copperbelt): Mineralogy, Geochemistry, and Potential Recovery of Critical Metals. *J. Geochem. Explor.* **2022**, *237*, 106987. [CrossRef]
72. Master, S.; Ndhlovu, N.M. Geochemical, Microtextural, and Mineralogical Studies of the Samba Deposit in the Zambian Copperbelt Basement: A Metamorphosed Paleoproterozoic Porphyry Cu Deposit. In *Ore Deposits: Origin, Exploration, and Exploitation*; Wiley: Hoboken, NJ, USA, 2019; pp. 37–55. ISBN 9781119290544.
73. Leteinturier, B.; Baker, A.J.M.; Bock, L.; Matera, J.; Malaisse, F. Copper and Vegetation at the Kansanshi Hill (Zambia) Copper Mine. *Belg. J. Bot.* **2001**, *134*, 41–50.
74. Vincens, A. Late Quaternary Vegetation History of the South-Tanganyika Basin. Climatic Implications in South Central Africa. *Palaeogeogr. Palaeoclim. Palaeoecol.* **1991**, *86*, 207–226. [CrossRef]
75. Key, R.M.; Liyungu, A.K.; Njamu, F.M.; Somwe, V.; Banda, J.; Mosley, P.N.; Armstrong, R.A. The Western Arm of the Lufilian Arc in NW Zambia and Its Potential for Copper Mineralization. *J. Afr. Earth Sci.* **2001**, *33*, 503–528. [CrossRef]
76. Van Wilderode, J.; El Desouky, H.A.; Elburg, M.A.; Vanhaecke, F.; Muchez, P. Metal Sources for the Katanga Copperbelt Deposits (DRC): Insights from Sr and Nd Isotope Ratios. *Geol. Belg.* **2014**, *17*, 137–147.
77. Azaraien, H.; Shahabpour, J.; Aminzadeh, B. Metallogenesis of the Sediment-Hosted Stratiform Cu Deposits of the Ravar Copper Belt (RCB), Central Iran. *Ore Geol. Rev.* **2017**, *81*, 369–395. [CrossRef]
78. El Desouky, H.A.; Muchez, P.; Cailteux, J. Two Cu-Co Sulfide Phases and Contrasting Fluid Systems in the Katanga Copperbelt, Democratic Republic of Congo. *Ore Geol. Rev.* **2009**, *36*, 315–332. [CrossRef]
79. Ettler, V.; Mihaljevič, M.; Kříbek, B.; Majer, V.; Šebek, O. Tracing the Spatial Distribution and Mobility of Metal/Metalloid Contaminants in Oxisols in the Vicinity of the Nkana Copper Smelter, Copperbelt Province, Zambia. *Geoderma* **2011**, *164*, 73–84. [CrossRef]
80. Gigler, G.M.; Kinnaird, J.A. Element Mobility in the Weathering Environment and Surface Vectors to Mineralisation—A Case Study from the Mashitu South Cu-Co Deposit, Katanga, Democratic Republic of Congo. *J. Geochem. Explor.* **2017**, *183*, 127–137. [CrossRef]
81. Fay, I.; Barton, M.D. Alteration and Ore Distribution in the Proterozoic Mines Series, Tenke-Fungurume Cu-Co District, Democratic Republic of Congo. *Min. Depos.* **2012**, *47*, 501–519. [CrossRef]
82. De Putter, T.; Mees, F.; Decrée, S.; Dewaele, S. Let's Talk Ore Deposits Supergene Copper Deposits and Minerals in the World-Class SHSC Deposits of the Central African Copperbelt (Katanga, DRC). In Proceedings of the Let's Talk Ore Deposits, Antofagasta, Chile, 26–29 September 2011.
83. Shabbir, Z.; Sardar, A.; Shabbir, A.; Abbas, G.; Shamshad, S.; Khalid, S.; Natasha; Murtaza, G.; Dumat, C.; Shahid, M. Copper Uptake, Essentiality, Toxicity, Detoxification and Risk Assessment in Soil-Plant Environment. *Chemosphere* **2020**, *259*, 127436. [CrossRef] [PubMed]
84. Freitas, H.; Prasad, M.N.V.; Pratas, J. Plant Community Tolerant to Trace Elements Growing on the Degraded Soils of São Domingos Mine in the South East of Portugal: Environmental Implications. *Environ. Int.* **2004**, *30*, 65–72. [CrossRef] [PubMed]
85. Juárez-Maldonado, A.; Tortella, G.; Rubilar, O.; Fincheira, P.; Benavides-Mendoza, A. Biostimulation and Toxicity: The Magnitude of the Impact of Nanomaterials in Microorganisms and Plants. *J. Adv. Res.* **2021**, *31*, 113–126. [CrossRef]
86. Cui, J.L.; Zhao, Y.P.; Lu, Y.J.; Chan, T.S.; Zhang, L.L.; Tsang, D.C.W.; Li, X. Distribution and Speciation of Copper in Rice (*Oryza sativa* L.) from Mining-Impacted Paddy Soil: Implications for Copper Uptake Mechanisms. *Environ. Int.* **2019**, *126*, 717–726. [CrossRef]
87. Lange, B.; Faucon, M.P.; Meerts, P.; Shutcha, M.; Mahy, G.; Pourret, O. Prediction of the Edaphic Factors Influence upon the Copper and Cobalt Accumulation in Two Metallophytes Using Copper and Cobalt Speciation in Soils. *Plant Soil* **2014**, *379*, 275–287. [CrossRef]
88. Bravo, S.; Amorós, J.A.; Pérez-de-los-Reyes, C.; García, F.J.; Moreno, M.M.; Sánchez-Ormeño, M.; Higueras, P. Influence of the Soil PH in the Uptake and Bioaccumulation of Heavy Metals (Fe, Zn, Cu, Pb and Mn) and Other Elements (Ca, K, Al, Sr and Ba) in Vine Leaves, Castilla-La Mancha (Spain). *J. Geochem. Explor.* **2017**, *174*, 79–83. [CrossRef]
89. Cameron, E.M.; Leybourne, M.I. Relationship between Groundwater Chemistry and Soil Geochemical Anomalies at the Spence Copper Porphyry Deposit, Chile. *Geochem. Explor. Environ. Anal.* **2005**, *5*, 135–145. [CrossRef]
90. El-Naggar, A.; Ahmed, N.; Mosa, A.; Niazi, N.K.; Yousaf, B.; Sharma, A.; Sarkar, B.; Cai, Y.; Chang, S.X. Nickel in Soil and Water: Sources, Biogeochemistry, and Remediation Using Biochar. *J. Hazard Mater.* **2021**, *419*, 126421. [CrossRef]
91. Kinraide, T.B.; Yermiyahu, U. A Scale of Metal Ion Binding Strengths Correlating with Ionic Charge, Pauling Electronegativity, Toxicity, and Other Physiological Effects. *J. Inorg. Biochem.* **2007**, *101*, 1201–1213. [CrossRef]

92. Moore, E.K.; Ostroverkhova, A.; Hummer, D.; Morrison, S.; Peralta, Y.; Spielman, S.J. The Influence of Oxygen and Electronegativity on Iron Mineral Chemistry throughout Earth's History. *Precambrian Res.* **2023**, *386*, 106960. [CrossRef]
93. Govett, G.J.S. Early Years in the Geochemical Prospecting Research Centre, Imperial College of Science and Technology, London: Exploration Geochemistry in Zambia in the Late 1950s; A Personal Recollection. *Geochem. Explor. Environ. Anal.* **2010**, *10*, 237–249. [CrossRef]
94. Kumar, V.; Pandita, S.; Singh Sidhu, G.P.; Sharma, A.; Khanna, K.; Kaur, P.; Bali, A.S.; Setia, R. Copper Bioavailability, Uptake, Toxicity and Tolerance in Plants: A Comprehensive Review. *Chemosphere* **2021**, *262*, 127810. [CrossRef] [PubMed]
95. Adriano, D.C. *Trace Elements in Terrestrial Environments*, 2nd ed.; Springer: Berlin/Heidelberg, Germany, 2001.
96. Anand, R.R.; Cornelius, M.; Phang, C. Use of Vegetation and Soil in Mineral Exploration in Areas of Transported Overburden, Yilgarn Craton, Western Australia: A Contribution towards Understanding Metal Transportation Processes. *Geochem. Explor. Environ. Anal.* **2007**, *7*, 267–288. [CrossRef] [PubMed]
97. Carrasco, T.L.; Girty, G.H. Identifying a Reference Frame for Calculating Mass Change during Weathering: A Review and Case Study Utilizing the C# Program Assessing Element Immobility and Critical Ratio Methodology. *Catena* **2015**, *125*, 146–161. [CrossRef]
98. Vela-Almeida, D.; Brooks, G.; Kosoy, N. Setting the Limits to Extraction: A Biophysical Approach to Mining Activities. *Ecol. Econ.* **2015**, *119*, 189–196. [CrossRef]
99. de Plaen, G.; Malaisse, F.; Brooks, R.R. The 'Copper Flowers' of Central Africa and Their Significance for Prospecting and Archaeology. *Endeavour* **1982**, *6*, 72–77. [CrossRef]
100. Roychoudhury, A.; Chakraborty, S. Cobalt and Molybdenum: Deficiency, Toxicity, and Nutritional Role in Plant Growth and Development. In *Plant Nutrition and Food Security in the Era of Climate Change*; Academic Press: Cambridge, MA, USA, 2022; pp. 255–270. [CrossRef]
101. Delhaye, G.; Lange, B.; Faucon, M.P.; Grandjean, C.; Mahy, G.; Meerts, P. Functional Traits of a Broad-Niched Metallophyte along a Toxicity Gradient: Disentangling Intra and Inter-Population Variation. *Environ. Exp. Bot.* **2018**, *156*, 240–247. [CrossRef]
102. Matakala, N.; Chirwa, P.W.; Mwamba, T.M.; Syampungani, S. Species Richness and Phytoremediation Potential of Mine Wastelands-Native Trees across the Zambian Copperbelt Region. *Heliyon* **2023**, *9*, e13585. [CrossRef]
103. Marastoni, L.; Sandri, M.; Pii, Y.; Valentinuzzi, F.; Brunetto, G.; Cesco, S.; Mimmo, T. Synergism and Antagonisms between Nutrients Induced by Copper Toxicity in Grapevine Rootstocks: Monocropping vs. Intercropping. *Chemosphere* **2019**, *214*, 563–578. [CrossRef]
104. Bakkaus, E.; Gouget, B.; Gallien, J.P.; Khodja, H.; Carrot, F.; Morel, J.L.; Collins, R. Concentration and Distribution of Cobalt in Higher Plants: The Use of Micro-PIXE Spectroscopy. *Nucl. Instrum. Methods Phys. Res. B* **2005**, *231*, 350–356. [CrossRef]
105. Baker, A.J.M.; Brooks, R.R. Terrestrial higher plants which hyperaccumulate metallic elements. A review of their distribution, ecology and phytochemistry. *Biorecovery* **1989**, *1*, 81–126.
106. Paton, A.; Brooks, R.R. A Re-Evaluation of Haumaniastrum Species as Geobotanical Indicators of Copper and Cobalt. *J. Geochem. Explor.* **1996**, *56*, 37–45. [CrossRef]
107. Verbruggen, N.; Hermans, C.; Schat, H. Molecular Mechanisms of Metal Hyperaccumulation in Plants. *New Phytol.* **2009**, *181*, 759–776. [CrossRef]
108. Smita, C.; Sugandha, S. Anandibai, 1 K E S Determination of Bioconcentration Factor (BCF) for Copper and Zinc in Pongamia Pinnata Plant and Blumea Malcolmii Plant Signifying Their Role as Bioindicators of Soil Contamination. *Res. J. Chem. Environ.* **2019**, *23*, 4.
109. Cole, M.M.; Le Roex, H.D.; Boshoff, A.F.; Buerger, A.D.; Mason, M.M.; Gadd, L.; Hughes, J.; Brown, R.C. The role of geobotany, biogeochemistry and geochemistry in mineral exploration in south west africa and botswana-A case history. *S. Afr. J. Geol.* **1978**, *81*, 277–317.
110. Li, M.S. Ecological Restoration of Mineland with Particular Reference to the Metalliferous Mine Wasteland in China: A Review of Research and Practice. *Sci. Total Environ.* **2006**, *357*, 38–53. [CrossRef]
111. Wang, Y.P.; Shi, J.Y.; Wang, H.; Lin, Q.; Chen, X.C.; Chen, Y.X. The Influence of Soil Heavy Metals Pollution on Soil Microbial Biomass, Enzyme Activity, and Community Composition near a Copper Smelter. *Ecotoxicol. Environ. Saf.* **2007**, *67*, 75–81. [CrossRef]
112. Klaes, B.; Wörner, G.; Thiele-Bruhn, S.; Arz, H.W.; Struck, J.; Dellwig, O.; Groschopf, N.; Lorenz, M.; Wagner, J.F.; Urrea, O.B.; et al. Element Mobility Related to Rock Weathering and Soil Formation at the Westward Side of the Southernmost Patagonian Andes. *Sci. Total Environ.* **2022**, *817*, 152977. [CrossRef] [PubMed]
113. Alekseenko, V.A.; Shvydkaya, N.V.; Alekseenko, A.V.; Machevariani, M.M.; Bech, J.; Pashkevich, M.A.; Puzanov, A.V.; Nastavkin, A.V.; Roca, N. Element Accumulation Patterns of Native Plant Species under the Natural Geochemical Stress. *Plants* **2021**, *10*, 33. [CrossRef] [PubMed]
114. Ginocchio, R.; León-Lobos, P.; Arellano, E.C.; Anic, V.; Ovalle, J.F.; Baker, A.J.M. Soil Physicochemical Factors as Environmental Filters for Spontaneous Plant Colonization of Abandoned Tailing Dumps. *Environ. Sci. Pollut. Res.* **2017**, *24*, 13484–13496. [CrossRef] [PubMed]
115. Weindorf, D.C.; Bakr, N.; Zhu, Y. Advances in Portable X-Ray Fluorescence (PXRF) for Environmental, Pedological, and Agronomic Applications. *Adv. Agron.* **2014**, *128*, 1–45. [CrossRef]

116. Deng, Y.; Wu, X.; Tian, Y.; Zou, Z.; Hou, X.; Jiang, X. Sharing One ICP Source for Simultaneous Elemental Analysis by ICP-MS/OES: Some Unique Instrumental Capabilities. *Microchem. J.* **2017**, *132*, 401–405. [CrossRef]
117. Kuznetsova, O.V.; Burmii, Z.P.; Orlova, T.V.; Sevastyanov, V.S.; Timerbaev, A.R. Quantification of the Diagenesis-Designating Metals in Sediments by ICP-MS: Comparison of Different Sample Preparation Methods. *Talanta* **2019**, *200*, 468–471. [CrossRef]
118. Harris, J.R.; Wilkinson, L.; Grunsky, E.C. Effective Use and Interpretation of Lithogeochemical Data in Regional Mineral Exploration Programs: Application of Geographic Information Systems (GIS) Technology. *Ore Geol. Rev.* **2000**, *16*, 107–143. [CrossRef]
119. Capistrant, P.L.; Hitzman, M.W.; Wood, D.; Kelly, N.M.; Williams, G.; Zimba, M.; Kuiper, Y.; Jack, D.; Stein, H. Geology of the Enterprise Hydrothermal Nickel Deposit, North-Western Province, Zambia. *Econ. Geol.* **2011**, *110*, 9–38. [CrossRef]
120. Kyser, K.; Lahusen, L.; Drever, G.; Dunn, C.; Leduc, E.; Chipley, D. Using Pb Isotopes in Surface Media to Distinguish Anthropogenic Sources from Undercover Uranium Sources. *Comptes Rendus-Geosci.* **2015**, *347*, 215–226. [CrossRef]
121. Chileshe, M.N.; Syampungani, S.; Festin, E.S.; Tigabu, M.; Daneshvar, A.; Odén, P.C. Physico-Chemical Characteristics and Heavy Metal Concentrations of Copper Mine Wastes in Zambia: Implications for Pollution Risk and Restoration. *J. For. Res.* **2020**, *31*, 1283–1293. [CrossRef]
122. Faucon, M.P.; Chipeng, F.; Verbruggen, N.; Mahy, G.; Colinet, G.; Shutcha, M.; Pourret, O.; Meerts, P. Copper Tolerance and Accumulation in Two Cuprophytes of South Central Africa: *Crepidorhopalon perennis* and *C. tenuis* (Linderniaceae). *Environ. Exp. Bot.* **2012**, *84*, 11–16. [CrossRef]
123. Bech, J.; Roca, N.; Tume, P. Hazardous Element Accumulation in Soils and Native Plants in Areas Affected by Mining Activities in South America. In *Assessment, Restoration and Reclamation of Mining Influenced Soils*; Academic Press: Cambridge, MA, USA, 2017; pp. 419–461. [CrossRef]
124. Brummer, J.J.; Woodward, G.D. A History of the 'Zambian Copper Flower', *Becium centraliafricanum* (*B. homblei*). *J. Geochem. Explor.* **1999**, *65*, 133–140. [CrossRef]
125. Kaninga, B.K.; Chishala, B.H.; Maseka, K.K.; Sakala, G.M.; Lark, M.R.; Tye, A.; Watts, M.J. Review: Mine Tailings in an African Tropical Environment—Mechanisms for the Bioavailability of Heavy Metals in Soils. *Environ. Geochem. Health* **2020**, *42*, 1069–1094. [CrossRef] [PubMed]
126. Shirmard, H.; Farahbakhsh, E.; Müller, R.D.; Chandra, R. A Review of Machine Learning in Processing Remote Sensing Data for Mineral Exploration. *Remote Sens. Environ.* **2022**, *268*, 112750. [CrossRef]
127. Dai, X.; Feng, H.; Xiao, L.; Zhou, J.; Wang, Z.; Zhang, J.; Fu, T.; Shan, Y.; Yang, X.; Ye, Y.; et al. Ecological Vulnerability Assessment of a China's Representative Mining City Based on Hyperspectral Remote Sensing. *Ecol. Indic.* **2022**, *145*, 109663. [CrossRef]
128. Manuel, R.; Brito, M.D.G.; Chichorro, M.; Rosa, C. Remote Sensing for Mineral Exploration in Central Portugal. *Minerals* **2017**, *7*, 184. [CrossRef]
129. Cloutis, E.A.; Hawthorne, F.C.; Mertzman, S.A.; Krenn, K.; Craig, M.A.; Marcino, D.; Methot, M.; Strong, J.; Mustard, J.F.; Blaney, D.L.; et al. Detection and Discrimination of Sulfate Minerals Using Reflectance Spectroscopy. *Icarus* **2006**, *184*, 121–157. [CrossRef]
130. Velasco, F.; Alvaro, A.; Suarez, S.; Herrero, J.M.; Yusta, I. Mapping Fe-Bearing Hydrated Sulphate Minerals with Short Wave Infrared (SWIR) Spectral Analysis at San Miguel Mine Environment, Iberian Pyrite Belt (SW Spain). *J. Geochem. Explor.* **2005**, *87*, 45–72. [CrossRef]
131. Dunagan, S.C.; Gilmore, M.S.; Varekamp, J.C. Effects of Mercury on Visible/near-Infrared Reflectance Spectra of Mustard Spinach Plants (Brassica Rapa P.). *Environ. Pollut.* **2007**, *148*, 301–311. [CrossRef]
132. Rathod, P.H.; Brackhage, C.; Van Der Meer, F.D.; Müller, I.; Noomen, M.F.; Rossiter, D.G.; Dudel, G.E. Spectral Changes in the Leaves of Barley Plant Due to Phytoremediation of Metals-Results from a Pot Study. *Eur. J. Remote Sen.* **2015**, *48*, 283–302. [CrossRef]
133. Rocchini, D.; Boyd, D.S.; Féret, J.B.; Foody, G.M.; He, K.S.; Lausch, A.; Nagendra, H.; Wegmann, M.; Pettorelli, N. Satellite Remote Sensing to Monitor Species Diversity: Potential and Pitfalls. *Remote Sen. Ecol. Conserv.* **2016**, *2*, 25–36. [CrossRef]
134. Foody, G.M.; Pal, M.; Rocchini, D.; Garzon-Lopez, C.X.; Bastin, L. The Sensitivity of Mapping Methods to Reference Data Quality: Training Supervised Image Classifications with Imperfect Reference Data. *ISPRS Int. J. Geoinf.* **2016**, *5*, 199. [CrossRef]
135. Nguyen, Q.H.; Ly, H.B.; Ho, L.S.; Al-Ansari, N.; Van Le, H.; Tran, V.Q.; Prakash, I.; Pham, B.T. Influence of Data Splitting on Performance of Machine Learning Models in Prediction of Shear Strength of Soil. *Math. Probl. Eng.* **2021**, *2021*, 4832864. [CrossRef]
136. Yaseen, Z.M. An Insight into Machine Learning Models Era in Simulating Soil, Water Bodies and Adsorption Heavy Metals: Review, Challenges and Solutions. *Chemosphere* **2021**, *277*, 130126. [CrossRef]
137. Abraham, A.; Pedregosa, F.; Eickenberg, M.; Gervais, P.; Mueller, A.; Kossaifi, J.; Gramfort, A.; Thirion, B.; Varoquaux, G. Machine Learning for Neuroimaging with Scikit-Learn. *Front. Neuroinform.* **2014**, *8*, 14. [CrossRef]
138. Verrelst, J.; Alonso, L.; Camps-Valls, G.; Delegido, J.; Moreno, J. Retrieval of Vegetation Biophysical Parameters Using Gaussian Process Techniques. *IEEE Trans. Geosci. Remote Sens.* **2012**, *50*, 1832–1843. [CrossRef]
139. Townsend, P.A.; Foster, J.R.; Chastain, R.A.; Currie, W.S. Application of Imaging Spectroscopy to Mapping Canopy Nitrogen in the Forest of the Central Appalachian Mountains Using Hyperion and AVIRIS. *IEEE Trans. Geosci. Remote Sens.* **2003**, *41*, 1347–1354. [CrossRef]
140. Shi, L.; Li, J.; Palansooriya, K.N.; Chen, Y.; Hou, D.; Meers, E.; Tsang, D.C.W.; Wang, X.; Ok, Y.S. Modeling Phytoremediation of Heavy Metal Contaminated Soils through Machine Learning. *J. Hazard. Mater.* **2023**, *441*, 129904. [CrossRef] [PubMed]

141. Mi, Y.; Zhou, J.; Liu, M.; Liang, J.; Kou, L.; Xia, R.; Tian, R.; Zhou, J. Machine Learning Method for Predicting Cadmium Concentrations in Rice near an Active Copper Smelter Based on Chemical Mass Balance. *Chemosphere* **2023**, *319*, 138028. [CrossRef] [PubMed]
142. Palansooriya, K.N.; Li, J.; Dissanayake, P.D.; Suvarna, M.; Li, L.; Yuan, X.; Sarkar, B.; Tsang, D.C.W.; Rinklebe, J.; Wang, X.; et al. Prediction of Soil Heavy Metal Immobilization by Biochar Using Machine Learning. *Environ. Sci. Technol.* **2022**, *56*, 4187–4198. [CrossRef] [PubMed]
143. Bhagat, S.K.; Tung, T.M.; Yaseen, Z.M. Development of Artificial Intelligence for Modeling Wastewater Heavy Metal Removal: State of the Art, Application Assessment and Possible Future Research. *J. Clean. Prod.* **2020**, *250*, 119473. [CrossRef]
144. Yang, H.; Huang, K.; Zhang, K.; Weng, Q.; Zhang, H.; Wang, F. Predicting Heavy Metal Adsorption on Soil with Machine Learning and Mapping Global Distribution of Soil Adsorption Capacities. *Environ. Sci. Technol.* **2021**, *55*, 14316–14328. [CrossRef]
145. Xu, X.; Ren, M.; Cao, J.; Wu, Q.; Liu, P.; Lv, J. Spectroscopic Diagnosis of Zinc Contaminated Soils Based on Competitive Adaptive Reweighted Sampling Algorithm and an Improved Support Vector Machine. *Spectrosc. Lett.* **2020**, *53*, 86–99. [CrossRef]
146. Li, P.; Hao, H.; Bai, Y.; Li, Y.; Mao, X.; Xu, J.; Liu, M.; Lv, Y.; Chen, W.; Ge, D. Convolutional Neural Networks-Based Health Risk Modelling of Some Heavy Metals in a Soil-Rice System. *Sci. Total Environ.* **2022**, *838*, 156466. [CrossRef]
147. Pyo, J.C.; Hong, S.M.; Kwon, Y.S.; Kim, M.S.; Cho, K.H. Estimation of Heavy Metals Using Deep Neural Network with Visible and Infrared Spectroscopy of Soil. *Sci. Total Environ.* **2020**, *741*, 140162. [CrossRef]
148. Bazoobandi, A.; Emamgholizadeh, S.; Ghorbani, H. Estimating the Amount of Cadmium and Lead in the Polluted Soil Using Artificial Intelligence Models. *Eur. J. Environ. Civ. Eng.* **2022**, *26*, 933–951. [CrossRef]
149. Duman, F.; Obali, O.; Demirezen, D. Seasonal Changes of Metal Accumulation and Distribution in Shining Pondweed (Potamogeton Lucens). *Chemosphere* **2006**, *65*, 2145–2151. [CrossRef] [PubMed]
150. Xu, K.; Su, Y.; Liu, J.; Hu, T.; Jin, S.; Ma, Q.; Zhai, Q.; Wang, R.; Zhang, J.; Li, Y.; et al. Estimation of Degraded Grassland Aboveground Biomass Using Machine Learning Methods from Terrestrial Laser Scanning Data. *Ecol. Indic.* **2020**, *108*, 105747. [CrossRef]