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# Bioaccumulation of potentially toxic elements by indigenous and exotic trees growing around a copper leaching plant in Mufulira, Zambia

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### Abstract

Potentially toxic elements (PTEs) from mining industries pollute the surrounding environment and threaten the health of communities. Worldwide, exotic and indigenous trees are being recommended for green belts to trap dust and thereby limit the dispersion of PTEs. This study compares the potential of exotic (Eucalyptus grandis and *E. camaldulensis*) and native (*Brachystegia longifolia*) tree species in Zambia to accumulate PTEs and evaluate their ability to biomonitor heavy metal pollution. Tree bark and leaf samples were collected from 10 trees per study species growing at the same site downwind from a copper-leaching plant. Thirty topsoil samples were collected one metre from each sampled tree trunk. Portable X-ray fluorescence was used to analyse the elemental composition and concentration of trace elements in plant and soil samples. Pollution indices were used to establish the status and degree of soil contamination, while the bioaccumulation factor determined the ability of the studied species to accumulate PTEs. Heavy metals, including Mn, Ni, Pb, Cd, Cu, Fe and Zn were detected across soil and biomass samples, with a significant variation between species and plant parts. The pollution indices established that the soil at the study site is highly contaminated with Cu. The concentration of the studied trace elements varied across species following the order *E. arandis* > *B. lonaifolia* > *E. camaldulensis* in both tree bark and leaves. Determined bioaccumulation factors indicated Cd, Mn and Zn accumulation abilities of all the studied species suggesting their biomonitoring and phytoremediation potential. This implies that the study species have the potential to biomonitor Cd, Mn and Zn. Furthermore, a higher concentration of Cu was detected in B. longifolia bark, suggesting that this tree species can be used to biomonitor Cu pollution attributed to emissions from industrial activities. This study presents new insights into improving the management of polluted environments through biomonitoring and bioaccumulation of PTEs which can guide the selection of appropriate species for greenbelts in industrial areas.

Keywords Copper, Emissions, Potentially toxic elements, Bioaccumulation factor, Biomonitoring

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### Introduction

There is an international debate on the use of exotic or native species to address the impacts of mining activities and the rehabilitation of post-mining forest ecosystems, (Ahirwal et al. 2016; Dutta and Agrawal 2003; Mondal and Singh 2022; Singh and Singh 1999).

The mineral beneficiation processes in the mining industry emit particulate matter comprising potentially toxic elements (PTEs), such as Cu, Cd, Pb and Ni (Kříbek et al. 2010; Lindahl 2014; Mapani et al. 2010). Beneficiation processes may range from deposit extraction to pyrometallurgy including concentrating, refining, roasting, leaching, crushing and smelting. (Eksteen et al. 2017). Potentially toxic elements may also emanate from mining waste disposal facilities, including tailings dams, waste rock dumps, and sludge dumps (Li and Yang 2008; Mapani et al. 2010; Ngole-Jeme and Fantke 2017; Olobatoke and Mathuthu 2016). Ultimately, dust dispersion assists the mobilisation of PTEs from mining activities into the environment, contaminating water bodies and soils (Lotfi et al. 2020; Olobatoke and Mathuthu 2016).

PTEs, which are trace elements may enter the plant tissue via roots or leaves (Fernández and Brown 2013; Lee et al. 2017). They penetrate through the foliar surfaces via cuticular cracks, lenticels and stomata (Shahid et al. 2016). However, foliar uptake of these elements depends on various factors, including particle size (Schreck et al. 2012) and plant species (Bahamonde et al. 2019). Eichert et al. (2008) demonstrated that stomata restrict the adsorption of trace elements in leaves. They reported adsorption of Cu nanoparticles (43 nm) in Vicia faba leaves, while large sized  $(1.1 \,\mu\text{m})$  particles could not penetrate. Similarly, Bahamonde et al. (2019) observed significant variations in the rate of foliar resorption in Cu, Fe, Mn, Al, Ti and B in Nothofagus pumilio and N. antarctica. On the other hand, trace elements are absorbed by the roots as ions in the soil. They are then taken up by root hairs and translocated through apoplastic and symplastic pathways, depositing them into the xylem tissue for upward transportation (Luo et al. 2016) to different plant parts (Page and Feller 2015). However, the extent and rate of translocation depends on several factors, including plant species and element speciation (Adriano 2001; Roberts et al. 2005).

The accumulation of PTEs has been reported in woody plants growing near mining areas in Mufulira and other towns of Zambia. Mulenga et al. (2022a) reported elevated levels of Cu, Zn, Fe and Mn in *Brachystegia longifolia* Benth naturally growing near mining activities in Mufulira. Kříbek et al. (2019) and Mihaljevič et al. (2018) observed a significant accumulation of Zn and Cu in tree growth rings of *Pinus oocarpa* and *P. Kesiya* attributed to mining activities in Kabwe and Kitwe. Furthermore, Ncube and Phiri (2015) recorded elevated Cd, Pb and Cr concentrations in *Eucalyptus closiana, P. Kesiya and P. oocarpa* and *P. kesiya* harvested from industrial areas in Ndola and Kitwe. However, these studies are confined to exotic species and the comparative uptake and accumulation of PTEs by indigenous and exotic tree species is not well understood.

Exotic trees i.e., *Eucalyptus grandis* W. Hill and *E. camaldulensis* Dehnh have been planted around a copper-leaching plant to serve as live fencing at a mine in Mufulira, Zambia. Native species to the Miombo woodlands are also naturally growing around the leaching plant. The trees on this site are being used as a greenbelt; trapping dust and possibly limiting the dispersion of PTEs across the surrounding areas, including a residential site within 1 km radius. This community is comprised of housing units, education and health facilities whose occupants could be affected by PTEs emanating from the leaching plant. However, there is a lack of comparative field-based scientific evidence on the potential and thereby, the effectiveness of these tree species in accumulating PTEs.

It is widely accepted that, the ability of plants to absorb and accumulate PTEs depends on many factors including plant species. This study compared the ability of *E. grandis, E. camaldulensis* and *B. longifolia* tree species to accumulate PTEs and to biomonitor heavy metal pollution.

A characteristic species of the Miombo woodlands, *B. longifolia*, is of high commercial value and widely distributed in Zambia, Zimbabwe, Tanzania, Malawi, Mozambique, Angola and the Democratic Republic of Congo (Jimu et al. 2017). *E. grandis* and *E. camaldulensis* are non-native tree species introduced in urban areas decades ago, mainly for timber production. Timber from all the three studied species is used for construction, furniture manufacturing and bioenergy production.

### Materials and methods

### Study area description

Mufulira, the study site, is located 43 km from Kitwe in the Copperbelt Province of Zambia (Fig. 1). This mining town is located at 12°31′ 59″ S, and 28° 13′ 55″ E and has one of the largest underground mines in Zambia. The average wind speed is 2.4 m/s and the main wind direction is towards the west (Mulenga et al. 2022a). This defines the areas to the west and east of the copper leaching plant as downwind and upwind, respectively.

Axenhamn & Simukanga (2005), Chifungula (2014) and Mulenga at al. 2022a observed high levels of dust emissions from the copper mine dispersed across the surrounding forests. Furthermore, Mulenga et al. (2022a) observed that areas up to 12 km downwind and 7 km upwind are contaminated with Cu emanating from mining activities.



Fig. 1 The location of the copper leaching plant in Mufulira

### The sampling strategy of the study

Tree bark was extracted at breast height (1.2 m) and topmost leaves harvested to constitute biomass samples. Ten (10) samples were extracted from 10 trees with a DBH ranging between 12 and 16 cm (*B. longifolia*), as well as 14 and 18 cm (*E. grandis* and *E. camaldulensis*). DBH capping was done to ensure that biomass samples are collected from trees within a similar age group and minimise the age influence on the generated data within and across tree species (Mulenga et al. 2022a). In addition, surface soil was collected at 10 cm depth, one metre away from each sampled standing tree trunk, facing the copper leaching plant (Dumčius 2016; Greece 2009; Zinkutė et al. 2006). In total, 30 soil samples were collected and analysed. All the samples were collected from the same site, about 500 m downwind of the copper leaching plant.

### Preparation and analysis of samples

The collected tree bark and leaves were washed under running deionised water and oven-dried at  $105\pm5$  °C to constant moisture content (Tokaliog<sup>\*</sup>lu et al. 2001; Yang et al. 2013). Oven-dried bark and leaves were ashed at 575 °C for 3 h (Buchmann et al. 2000; Enders and

Lehmann 2012; Ge et al. 2008; Shen et al. 2015; Väisänen et al. 2008). Soil samples were pulverised by hand, sieved by vibration and oven-dried at  $105\pm5$  °C to constant moisture content (Ichikawa and Nakamura 2016; Nuch-dang et al. 2018; Tavares et al. 2019). Light pulverisation was performed to avoid crushing or milling stones, which could affect the soils' chemical composition and then mechanically sieved through a 150 µm sieve, obtaining the fine particle sizes suitable for elemental analysis (Demir et al. 2008; Ichikawa and Nakamura 2016; Mzyk et al. 2002; Yagura et al. 2019).

A Thermo Niton XL3t GOLDD+ (pXRF-portable X-ray fluorescence) was used to analyse the composition and concentration of PTEs in all samples. Portable X-ray fluorescence analysis offers a quick and reliable alternative or complement to traditional techniques (ICP-AES, ICP-MS, ICP-OES and AAS) producing relative concentrations (counts of fluorescent photons per second, cps) and allowing for extensive, inexpensive and faster analysis regimes (Al Maliki et al. 2017; Congiu et al. 2013; Marcos et al. 2011; Rouillon and Taylor 2016). Furthermore, this method has been implemented in different studies evaluating soil (Congiu et al. 2013; Janotková et al. 2013; Rizvi et al. 2020; Rouillon and Taylor 2016) and plant (Chojnacka et al. 2018; Elzain et al. 2016; Marguí et al. 2005; Mulenga et al. 2022a; Roquette et al. 2023) trace element contamination. Soil pH was determined through potassium chloride (KCl) on air-dried soil (Mulenga et al. 2022a).

## Analysis of soil pollution status and degree of soil contamination

The degree and status of soil contamination were analysed through the Enrichment factor (EF) and Geoaccumulation index (GI). These indices are suitable to assess anthropogenic-induced soil pollution (Kowalska et al. 2018). The GI and EF pollution indices were calculated using Eq. 1 and Eq. 2, respectively (Sutherland 2000):

$$GI = log_2 \left[ \frac{Sample M_c}{1.5 * GB} \right] [1]$$
$$EF = \left\{ \frac{Sample \left[ \frac{M_c}{N_e} \right]}{WASV \left[ \frac{M_c}{N_e} \right]} \right\} [2]$$

Where  $M_c$ : total concentration of trace element in the soil sample, GB: World average shale values (WASV) or trace element background value and Ne: normalization element from PTEs with low soil occurrence variability, e.g. Al, Ca, Fe, Mn, Ti or Si (Mazurek et al. 2017). The factor 1.5 in the calculation of GI takes into account fluctuations in geochemical background values relating to natural weathering or lithogenic effects (Abdullah et al. 2020; Kowalska et al. 2018; Nowrouzi and Pourkhabbaz 2015).

The WASV (Onjefu et al. 2020) were used in this study for lack of pre-industrial geochemical background values in the study area (Mulenga 2022). WASV values of 45 mg/ kg (Cu), 47,200 mg/kg (Fe), 850 mg/kg (Mn), 68 mg/kg (Ni), 20 mg/kg (Pb), 94 mg/kg (Zn), 5700 mg/kg (Ti) and 16 mg/kg (Cd) were used to calculate GI and EF. These

 Table 1
 <sup>1</sup>Soil contamination criteria based on GI and EF.

Enrichment factor		Geoaccumulation index	
Classification	Degree of soil enrichment	Classification	Degree of soil contamination
0<2	Deficient	GI < 0	Unpolluted
2 < EF < 5	Moderate	1≤GI<2	Moderately polluted
5 < EF < 20	Significant	$3 \le GI < 4$	Strongly polluted
20 < EF < 40	Very significant	4≤GI<5	Strong to very strong polluted
EF > 40	Extremely significant	GI≥5	Very strongly polluted

<sup>1</sup> Adapted from Abdullah et al. (2020) and Onjefu et al. (2020).

values have been used and recommended in various studies (Kowalska et al. 2018; Mulenga et al. 2022a; Nowrouzi and Pourkhabbaz 2015; Onjefu et al. 2020) for soil pollution assessments in territories lacking site-specific geochemical references, including mining environments. Titanium was used as normalization element because of its low occurrence variability across the soil samples.

The classification and interpretation of the pollution indices obtained from Eq. 1 and Eq. 2 are outlined in Table 1. EF values ranging between 0.5 and 1.5 are caused by variations in metal concentration in the soil due to natural weathering. If EF is larger than 1.5 the fluctuation of metal content in the soil can be attributed to anthropogenic activities (Abdullah et al. 2020; Kowalska et al. 2018; Nowrouzi and Pourkhabbaz 2015).

# Analysis of potentially toxic element bioaccumulation in trees

The bioaccumulation factor (BAF) was used to determine the potential of *E. grandis, E. camaldulensis* and *B. longifolia* to accumulate PTEs. BAF is a measure of the ability of a plant species to accumulate specific trace elements in its tissues and one of the factors used in identifying species for phytoremediation strategies and biomonitoring. It is calculated as a ratio between the elemental composition in plant shoots or leaves and the respective total element concentration in the soil or growth medium, Eq. 3 (Molnár et al. 2020).

$$BAF = C_p/C_{so}[3]$$

Where  $C_p$ : element content in leaves or shoots and  $C_{so}$ : total content of an element in the growth medium or soil. Plants with element BAF values larger than one are regarded as accumulators, capable of compartmentalizing specified trace elements in the their tissues (Cruzado-Tafur et al. 2021).

### Statistical data analysis

Analysis of variance (ANOVA) was conducted to establish variations on the concentration of PTEs in biomass samples of the studied species. Significant variations are reported at p<0.05. The graphs and statistics were produced using a statistical package, R (R Core Team, 2022).

### **Results and discussion**

### Degree and source of soil contamination

This study evaluated PTEs that were detected across the three sample types. A total number of seven PTEs (Mn, Ni, Pb, Cd, Cu, Fe and Zn) were detected across the sample types. There was a significant variation on the concentration of different PTEs in the soil. The average concentration accounted for 30,388 mg/kg (Fe), 2912 mg/

kg (Cu), 701 mg/kg (Mn), 67 mg/kg (Ni), 57 mg/kg (Zn), 26 mg/kg (Cd) and 25 mg/kg (Pb).

The soil pollution assessments carried out indicates that the study site is mostly polluted with Cu (Fig. 2). The geoaccumulation index, which compares the current concentration of trace elements to pre-industrial levels in the soil shows very strong soil contamination (GI $\geq$ 5) around the copper leaching plant. Furthermore, the EF pollution index, which measures both soil pollution status and possible source of enrichment confirmed significant Cu pollution (EF>20) around the leaching plant, driven by anthropogenic activities (EF>1.5).

These results confirm the dispersion of dust from the copper leaching plant in Mufulira and demonstrate the impact of anthropogenic activities, including mining on forest soil in the surrounding landscape (Li and Yang 2008; Mapani et al. 2010; Ngole-Jeme and Fantke 2017; Olobatoke and Mathuthu 2016). Similar results have been reported in different mining towns in Zambia and other mining countries (Ettler et al. 2022; Ikenaka et al. 2014; Kříbek et al. 2019; Matakala et al. 2023; Mihaljevič et al. 2018; Van Der Ent et al. 2020). In Zambia, Cu and Co soil contamination was observed in Luanshya (Ettler et al. 2022), Pb-Zn soil pollution in Kabwe (Kříbek et al. 2019) and Cu soil enrichment in Kitwe (Mihaljevič et al.

Т

80

60

2018), all attributed to emission dispersion from mining activities.

The soil pH recorded from all the 30 soil samples on the study site ranged from 3.45 to 4.36, confirming earlier studies in the area noting that forest soil in Mufulira and the surrounding is strongly acidic (Mulenga et al. 2022a; Tsuji et al. 2005).

### Concentration of potentially toxic elements in plants

The concentration of PTEs varied significantly based on tree species and plant organ (Fig. 3). Mn, Zn and Pb concentration was higher in leaves than tree bark, for all studied tree species. On the other hand, Fe, Ni, Cd and Cu varied significantly among tree species and plant organs. In *B. longifolia*, Cu, Cd and Ni were significantly higher in tree bark than leaves. A similar trend was observed in *E. grandis* for Cu, Fe and Ni.

The observed heavy metal concentration behaviour especially in *B. longifolia* can be attributed to Cu adsorption through the stem because the bark of this tree species is grooved with deep vertical fissures (Storrs 1995). Furthermore, Storrs (1995) noted that the bark is ridged in long strips, which crack horizontally resulting in square flakes and the grooves on the stem look like claw marks. On the other hand, the bark of *E. camaldulensis* 



Fig. 2 Status and degree of soil contamination based on GI and EF of each studied PTEs, n = 10. The error bars represent the standard error of the mean



Fig. 3 Concentration of PTEs in tree bark and leaves, n = 10. The different letters indicate mean significant differences at 5% of significance between species. B.L: *B. longifolia*, E.C: *E. camaldulensis* and E.G: *E. grandis*. The error bars represent the standard error of the mean

is smooth with rough and loose slabs at the base (Ali and Usman 2022; Sani et al. 2014).

The enrichment factor of over 1.5 for Cu in Fig. 2 shows that Cu soil contamination on this study site is instigated by anthropogenic activities. Since copper-leaching is the only anthropogenic activity at the study site, Cu pollution on this site can be attributed to the dispersion of mineral enriched dust from the copper mine. Consequently, more mineral particles are trapped and adsorbed into the bark from the atmosphere by highly fissured bark.

Similar results have been reported in other studies where tree bark passively accumulated PTEs from the atmosphere and served as an active transport surface, exchanging these elements longitudinally and laterally (Dogan et al. 2014; Luo et al. 2016; Page et al. 2006; Ponette-González 2021; Rodríguez et al. 2018). Furthermore, the effectiveness of tree bark in trace element adsorption and the potential of biomonitoring atmospheric pollution is strongly attributed to its surface morphology, or fissures and lenticel size and distribution (Alatou and Sahli 2019; Caldana et al. 2023; Catinon et al. 2009; Chrabąszcz and Mróz 2017; Drava et al. 2017; Guéguen et al. 2012; Olajire and Ayodele 2003; Reimann et al. 2007). These results demonstrate that *B. longifolia* bark can be used for biomonitoring atmospheric Cu pollution. It further suggests that sampling tree bark rather than leaves offers a better sampling option in assessing the concentration of Cu in *B. longifolia* and possibly other tree species, attributed to dust emissions.

It is clearly demonstrated in Fig. 3 that the native B. longifolia leaves recorded more Zn and Mn than E. camaldulensis and E. grandis, respectively. The concentration of Cd, Ni and Cu were significantly higher in B. longifolia tree bark than in leaves. The ability of B. longifolia to absorb more Mn and Zn has previously been attributed to adaptation of this tree species to its native acidic Miombo woodlands (Mulenga et al. 2022b). Comparable results have been reported in Pseudotsuga menziesii (Radwan et al. 1979), as well as Populus trochocarpa, Tsuga heterophylla, P. Menziesii and P. Nigra (Zasoski et al. 1990), grown in acidic growth medium. However, the concentration of PTEs in Fig. 3 shows elevated levels of Cu, Mn and Cd in all species and Zn in E. camaldulensis and B. longifolia. These concentration levels could be toxic and impact on tree growth and forest productivity. Critical toxicity varies depending on plant species, but average limits are >10 mg/kg (Cd), > 120 mg/kg (Zn), > 25 mg/kg (Cu) and >200 mg mg/kg (Mn) for non-hyperaccumulators (Emamverdian et al. 2015; Krämer 2010; Sharma et al. 2016).

### Bioaccumulation of potentially toxic elements in tree bark and leaves

The bioaccumulation factor is a measure of the ability of plant species to accumulate specific trace elements in plants parts. Figure 4 shows that the studied species can take up and compartmentalize selected trace elements in the bark and leaf tissues in varying quantities. The bioaccumulated elements include Cd, Mn, and Zn. The results show that Mn and Zn accumulates more in the leaf than in tree bark tissue for all studied species. Conversely, Cd accumulates more in tree bark than in leaves.

Furthermore, Fig. 4 demonstrates significant differences in the bioaccumulation of trace elements across tree species and plant parts. *E. grandis* accumulated the highest levels of Cd, Mn and Zn compared to *E. camaldulensis* and *B. longifolia*. The average bioaccumulation levels in *E. grandis* followed the order Mn>Cd>Zn for both leaves and tree bark. However, the bioaccumulation order of PTEs in *E. camaldulensis* was Zn>Mn>Cd (leaves) and Zn>Cd>Mn (bark). Finally, variations in the bioaccumulation patterns of PTEs in *B. longifolia* followed the order Mn>Zn>Cd (leaves) and Mn>Cd>Zn (bark).

These results confirm an earlier study that demonstrated that *B. longifolia* can accumulate Mn and Zn (Mulenga et al. 2022a). Furthermore, the results demonstrates the potential of the studied species in phytoremediation, restoring Mn, Cd and Zn contaminated landscapes. Other studies have also observed several woody plants accumulating selected PTEs including Cd (Amirahmadi et al. 2020; Chaplygin et al. 2020), Mn (Fernando et al. 2006; Millaleo et al. 2010; Yang et al. 2008) and Zn (Chaplygin et al. 2020; Shi et al. 2011), attributed to the acidic growth medium (Shaari et al. 2024), which instigates the transformation from insoluble to plant available forms of these elements (Li et al. 2014). However, the ability of plants to accumulate PTEs depend on many factors, including species and trace elements.



Fig. 4 Bioaccumulation of PTEs in plants, n = 10. The horizontal line shows the bioaccumulation limit. PTEs with values exceeding this line can accumulate in the respective tree species. The error bars represent the standard error of the mean

Matakala et al. (2023) studied the ability of native woody species naturally growing on tailing dams to accumulate trace elements in leaves and roots. They observed that *Annona senegalensis*, *Parinaric curatellifolia* and *Dombeya rutundilifolia* could accumulate Ni, Co, Cu, Mo and Cr well. Conversely, these species could not accumulate Ba, B, Zn and Mn. Comparable results have been reported in several other studies (Collin et al. 2022; El-Khatib et al. 2020; Pietrelli et al. 2022; Robin et al. 2022; Thanh-Nho et al. 2019; Uddin et al. 2021).

The fraction of PTEs absorbed by root cells and translocated throughout the plant depends on the plant's uptake characteristics, namely the selectivity/exclusion or accumulation (White 2012). Therefore, the inability of the studied species to accumulate Cu, Ni, Pb and Fe could be attributed to selectivity/exclusion mechanisms (Atkinson and Guerinot 2010; Fernando and Lynch 2015; Rietra et al. 2017; Schulz 2010; Sharma et al. 2016).

In an extensive review, Mulenga et al. (2020) pointed out that different trace elements have varying effects on plants depending on the quantities absorbed and their subsequent role in biochemical and physiological processes in plant tissues. Notably, only a few studies have gone further to establish the effect of these elements on tree growth and utility properties to assess the productivity of forests within the reach of emissions from mining activities. Understanding the impact of mining activities on forest productivity can help to formulate strategies aimed at addressing sustainable mining challenges.

### Absorption and translocation of trace elements in plants

The uptake of trace element ions from the soil solution into plant roots is facilitated by proteins referred to as transporters. The main transporters include the family members of heavy metal ATPases (adenosine triphosphate) (HMA), zinc-iron permease (ZIP) and natural resistance-associated macrophage protein (NRAMP) (Shi et al. 2019). These are localized in different parts of the root cell compartments. Each family member of these transporters participates in the uptake and translocation of different trace elements depending on their affinity (Milner et al. 2014). Studies on Nocatee caerulescens and Arabidopsis thaliana show that AtZIP2 absorbs and translocates  $Mn^{2+}/Zn^{2+}$  into the root cells. Furthermore, NcZNT1, a homolog of AtZIP4 absorbs and transport  $Zn^{2+}$  and  $Cd^{2+}$ , while IRT1 is involved in the uptake of  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Fe^{2+}$  and  $Fe^{3+}$  (Lin et al. 2016; Lombi et al. 2002). All these transporters are localized in the plasma membrane.

NRAMP family members specialize in absorbing bivalent ions into the root stellar cells, while HMAs translocate both divalent and monovalent ions throughout the plants (Milner et al. 2014). HMAs (AtHMA1, AtHMA2 and AtHMA4) facilitates the translocation ions into shoots from roots (Cun et al. 2014).

Other trace element ions form complexes with phytochelatins (Kozhevnikova et al. 2014). These complexes are then absorbed by root cells through oligopeptide transporters and ATP-binding cassette (Richau et al. 2009). However, Luo et al. (2016) argued that the mechanisms governing the uptake and translocation of potentially toxic element ions in woody plants is not well established. They suggested that the inflow of toxic elements into woody roots is greater than herbaceous roots. This position was earlier supported by He et al. (2011) observed a 100 times lower  $Cd^{2+}$  inflow into the roots of herbaceous *Triticum aestivum* than woody *Populus tremula* and *Populus alba*. However, it is widely accepted that the uptake and translocation of trace element ions in plants depends on many factors, including transporters and species.

The selective ability of transporters in the uptake of trace element ions from the soil solution into the root cell and their subsequent translocation throughout the plant gives rise to significant variations in the concentration of these elements in plant tissues. Consequently, elements with a higher distribution network are absorbed and translocated in large quantities from the growth medium, possibly explaining the variations in the bioaccumulation or hyperaccumulation potential of different plant species. It is demonstrated in Fig. 4 that despite Cu and Fe recording higher concentration in the soil, the concentration of these elements in the tissues of studied tree species was lower than the growth medium. Future studies should establish and compare the expression of these transporters across the studied species, and possibly other tree species with phytoremediation potential. This would help fast-track the identification of accumulators and hyperaccumulators of PTEs based on transporters, for the benefit phytoremediation programmes.

### Conclusions

The aim of this study was to compare the potential of the three tree species to accumulate PTEs and evaluated the ability of the tree species in biomonitoring heavy metal pollution. Pollution indices (EF and GI) were employed on soil samples to establish the status and degree of contamination, while the bioaccumulation factor was used for biomass samples (bark and leaves) from 10 trees to assess bioaccumulation and biomonitoring potential. The study detected seven PTEs across soil and biomass samples, which included Mn, Ni, Pb, Cd, Cu, Fe and Zn. The pollution indices established that the soil on the study site is highly polluted with Cu, confirming the dispersion of dust from the copper leaching plant and demonstrated the serious impact of mining related anthropogenic causes on the study site. Of the three tree species, E. grandis had the highest accumulation of heavy metals followed by B. longifolia and E. camaldulensis; however, the general concentration varies based on specific plant parts (bark or leaves). Furthermore, the study showed that the tree species can accumulate selective trace elements in the bark and leaves at varying quantities, with elements such as Cd, Mn, and Zn being common. It also demonstrated that B. longifolia bark can be used to biomonitor Cu dust emissions attributed to industrial activities. This study delivers new insights in improving the management of polluted environment through biomonitoring and phytoremediation as the findings from this study can guide policy on species selection when establishing greenbelts in mining and other industrial areas. Specifically, the study shows that native tree species naturally growing in polluted landscapes have the potential in biomonitoring metal pollution and are also possible candidates in phytoremediation strategies.

### Acknowledgements

The authors would like to thank the Copperbelt University for facilitating sample collection, Mopani Copper Mines for the permission to sample in their mining protected area.

DROR acknowledges the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for research fellowship (Grant number 2020/04608-7, 2018/22914-8 and 2017/50085-3).

#### Author contributions

CM: Study conceptualization, sample collection and data analysis. CM, DP, OR and MM: Study design, results interpretation and manuscript drafting. MM: Mobilised resources and supervised the study. MM: Manuscript editing. All authors read and approved the final manuscript.

### Funding

The Department of Forest and Wood Science at Stellenbosch University provided funds for this study. However, the department or the university did not have a role in the design of the study and data collection, analysis, interpretation, and manuscript writing.

### Data availability

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

### Declarations

Ethics approval and consent to participate Not applicable.

### Consent for publication

Not applicable.

### **Competing interests**

The authors declare that they have no competing interests.

Received: 30 May 2023 / Accepted: 28 June 2023 Published online: 10 July 2023

### References

- Abdullah C, li M, Sah MRA, Haris H (2020) Geoaccumulation Index and Enrichment factor of Arsenic in Surface Sediment of Bukit Merah Reservoir, Malaysia. Tripical Life Sciences Research 31(3):109–125
- Adriano DC (2001) Trace Elements in Terrestrial environments: Biogeochemistry, Bioavailability and Risks of Metals. Journal of Environmental Quality, vol

32. Second, Issue 1). Springer-Verlag New York. https://doi.org/10.2134/ jeq2002.3740

- Ahirwal J, Maiti SK, Singh AK (2016) Ecological restoration of Coal Mine-Degraded Lands in Dry Tropical Climate: what has been done and what needs to be done? Environ Qual Manage 26(1):25–36. https://doi.org/10.1002/ tqem.21481
- Al Maliki A, Al-lami AK, Hussain HM, Al-Ansari N (2017) Comparison between inductively coupled plasma and X-ray fluorescence performance for pb analysis in environmental soil samples. Environ Earth Sci 76(12):1–7. https:// doi.org/10.1007/s12665-017-6753-z

Alatou H, Sahli L (2019) Using tree leaves and barks collected from contaminated and uncontaminated areas as indicators of air metallic pollution. Int J Phytoremediation 21(10):985–997. https://doi.org/10.1080/15226514.2019. 1583723

- Ali A, Usman MI (2022) Hepatocurative Properties of Eucalyptus camaldulensis stem bark extract. East Afr Scholars J Agric Life Sci 5(7):146–150. https://doi. org/10.36349/easjals.2022.v05i07.003
- Amirahmadi E, Hojjati SM, Kammann C (2020) Applied sciences the potential E ff ectiveness of Biochar Application to reduce soil cd bioavailability and encourage Oak Seedling Growth. Appl Sci 10(3410):1–13
- Atkinson A, Guerinot LM (2010) Metal Transport. In A. S. Murphy, W. Peer, & B. Schulz (Eds.), *The Plant Plasma Membrane* (p. 303). https://doi.org/10.1017/CBO9781107415324.004

Bahamonde HA, Fernández V, Gyenge J, Mattenet F, Peri PL (2019) Essential nutrient and Trace element Foliar Resorption of two co-existing Nothofagus species grown under different environmental conditions in Southern Patagonia. Front Plant Sci 10(November):1–13. https://doi.org/10.3389/fpls.2019.01542

Buchmann JH, De Souza Sarkis JE, Rodrigues C (2000) Determination of metals in plant samples by using a sector field inductively coupled plasma mass spectrometer. Sci Total Environ 263(1–3):221–229. https://doi.org/10.1016/ S0048-9697(00)00710-5

- Caldana CRG, Hanai-Yoshida VM, Paulino TH, Baldo DA, Freitas NP, Aranha N, Vila MMDC, Balcão VM, Oliveira Junior JM (2023) Evaluation of urban tree barks as bioindicators of environmental pollution using the X-ray fluorescence technique. Chemosphere 312:137257. https://doi.org/10.1016/j. chemosphere.2022.137257
- Catinon M, Ayrault S, Clocchiatti R, Boudouma O, Asta J, Tissut M, Ravanel P (2009) The anthropogenic atmospheric elements fraction: a new interpretation of elemental deposits on tree barks. Atmos Environ 43(5):1124–1130. https:// doi.org/10.1016/j.atmosenv.2008.11.004
- Chaplygin V, Mandzhieva S, Litvinov Y, Kravtsova N, Sherstnev A, Chernikova N, Deryabkina I (2020) Zinc and cadmium accumulation in different parts of wild plants of the Asteraceae family and Triticum aestivum. E3S Web of Conferences, 169, 0–5. https://doi.org/10.1051/e3sconf/202016901003
- Chojnacka K, Samoraj M, Tuhy L, Michalak I, Mironiuk M, Mikulewicz M (2018) Using XRF and ICP-OES in biosorption studies. Molecules 23(8). https://doi. org/10.3390/molecules23082076
- Chrabąszcz M, Mróz L (2017) Tree bark, a valuable source of information on air quality. Pol J Environ Stud 26(2):453–466. https://doi.org/10.15244/ pjoes/65908
- Collin S, Baskar A, Geevarghese DM, Ali MNVS, Bahubali P, Choudhary R, Lvov V, Tovar GI, Senatov F, Koppala S, Swamiappan S (2022) Bioaccumulation of lead (pb) and its effects in plants: a review. J Hazard Mater Lett 3(July):100064. https://doi.org/10.1016/j.hazl.2022.100064
- Congiu A, Perucchini S, Cesti P (2013) Trace metal contaminants in sediments and soils: Comparison between ICP and XRF quantitative determination. *E3S Web of Conferences*, 1, 1–4. https://doi.org/10.1051/e3sconf/20130109004
- Cruzado-Tafur E, Bierla K, Torr L (2021) Growing in Soils contaminated by Mining Environmental Liabilities in the peruvian Andes. Plants 10(241):1–23. https:// doi.org/10.3390/plants10020241
- Cun P, Sarrobert C, Richaud P, Chevalier A, Soreau P, Auroy P, Gravot A, Baltz A, Leonhardt N, Vavasseur A (2014) Modulation of Zn/Cd P1B2-ATPase activities in Arabidopsis impacts differently on Zn and Cd contents in shoots and seeds. Metallomics 6(11):2109–2116. https://doi.org/10.1039/c4mt00182f
- Demir F, Simsek O, Budak G, Karabulut A (2008) Effect on particle size to emitted X-ray intensity in pellet cement sample analyzed with WDXRF spectrometer. Instrum Sci Technol 36(4):410–419. https://doi. org/10.1080/10739140802151689
- Dogan Y, Unver MC, Ugulu I, Calis M, Durkan N (2014) Heavy metal accumulation in the bark and leaves of juglans regia planted in artvin city, Turkey. Biotechnol Biotechnol Equip 28(4):643–649. https://doi.org/10.1080/13102818.2014.94 7076

- Drava G, Brignole D, Giordani P, Minganti V (2017) The bark of the branches of holm oak (Quercus ilex L.) for a retrospective study of trace elements in the atmosphere. Environ Res 154(January):291–295. https://doi.org/10.1016/j. envres.2017.01.022
- Dumčius A (2016) Selection of investigation methods for heavy metal pollution on soil and sediments of water basins and river bottoms: a review. https://doi. org/10.6001/ekologija.v57i1.1307. May
- Dutta RK, Agrawal M (2003) Restoration of opencast coal mine spoil by planting exotic tree species: a case study in dry tropical region. Ecol Eng 21(2):143– 151. https://doi.org/10.1016/j.ecoleng.2003.10.002
- Eichert T, Kurtz A, Steiner U, Goldbach HE (2008) Size exclusion limits and lateral heterogeneity of the stomatal foliar uptake pathway for aqueous solutes and water-suspended nanoparticles. Physiol Plant 134(1):151–160. https://doi.org/10.1111/j.1399-3054.2008.01135.x
- Eksteen JJ, Oraby EA, Tanda BC (2017) A conceptual process for copper extraction from chalcopyrite in alkaline glycinate solutions. Miner Eng 108:53–66. https://doi.org/10.1016/j.mineng.2017.02.001
- El-Khatib AA, Barakat NA, Youssef NA, Samir NA (2020) Bioaccumulation of heavy metals air pollutants by urban trees. Int J Phytoremediation 22(2):210–222. https://doi.org/10.1080/15226514.2019.1652883
- Elzain AH, Ebrahim AM, Eltoum A (2016) Comparison between XRF, PIXE and ICP-OES Techniques Applied for analysis of some Medicinal plants. IOSR J Appl Chem (IOSR-JAC 9(4):6–12. https://doi.org/10.9790/5736-0904010612
- Emamverdian A, Ding Y, Mokhberdoran F, Xie Y (2015) Heavy metal stress and some mechanisms of plant defense response. *Scientific World Journal*, 1(2015), 1–18. https://doi.org/10.1155/2015/756120
- Enders A, Lehmann J (2012) Comparison of wet-digestion and dry-ashing methods for total elemental analysis of Biochar. Commun Soil Sci Plant Anal 43(7):1042–1052. https://doi.org/10.1080/00103624.2012.656167
- Ettler V, Mihaljevič M, Drahota P, Kříbek B, Nyambe I, Vaněk A, Penížek V, Sracek O, Natherová V (2022) Cobalt-bearing copper slags from Luanshya (Zambian Copperbelt): Mineralogy, geochemistry, and potential recovery of critical metals. J Geochem Explor 237(February). https://doi.org/10.1016/j. gexplo.2022.106987
- Fernández V, Brown PH (2013) From plant surface to plant metabolism: the uncertain fate of foliar-applied nutrients. Front Plant Sci 4(JUL). https://doi. org/10.3389/fpls.2013.00289
- Fernando DR, Lynch JP (2015) Manganese phytotoxicity: new light on an old problem. Ann Botany 116(3):313–319. https://doi.org/10.1093/aob/mcv111
- Fernando DR, Bakkaus EJ, Perrier N, Baker AJM, Woodrow IE, Batianoff GN, Collins RN (2006) Erratum: Manganese accumulation in the leaf mesophyll of four tree species: A PIXE/EDAX localization study (New Phytologist (2006) 171 (751–758)). New Phytologist, 172(2), 375–376. https://doi. org/10.1111/j.1469-8137.2006.01883.x
- Ge C, Lao F, Li W, Li Y, Chen C, Qiu Y, Mao X, Li B, Chai Z, Zhao Y (2008) Quantitative analysis of metal impurities in carbon nanotubes: efficacy of different pretreatment protocols for ICPMS spectroscopy. Anal Chem 80(24):9426–9434. https://doi.org/10.1021/ac801469b

Greece H (2009) General procedure for the sampling of soils

- Guéguen F, Stille P, Lahd Geagea M, Boutin R (2012) Atmospheric pollution in an urban environment by tree bark biomonitoring – part I: Trace element analysis. Chemosphere 86(10):1013–1019. https://doi.org/10.1016/j. chemosphere.2011.11.040
- He J, Qin J, Long L, Ma Y, Li H, Li K, Jiang X, Liu T, Polle A, Liang Z, Luo Z, Bin (2011) Net cadmium flux and accumulation reveal tissue-specific oxidative stress and detoxification in Populus x canescens. Physiol Plant 143(1):50–63. https://doi.org/10.1111/j.1399-3054.2011.01487.x
- Ichikawa S, Nakamura T (2016) Solid sample preparations and applications for X-Ray fluorescence analysis. Encyclopedia of Analytical Chemistry 1–22. https://doi.org/10.1002/9780470027318.a9562
- Ikenaka Y, Nakayama SMM, Muzandu K, Choongo K, Teraoka H, Mizuno N, Ishizuka M (2014) Heavy metal contamination of soil and sediment in Zambia. Heavy Metal Contamination of Water and Soil: Analysis Assessment and Remediation Strategies 4(December):109–128. https://doi.org/10.1201/b16566
- Janotková I, Prokeš L, Vaculovič T, Holá M, Pinkas J, Steffan I, Kubáň V, Kanický V (2013) Comparison of inductively coupled plasma optical emission spectrometry, energy dispersive X-ray fluorescence spectrometry and laser ablation inductively coupled plasma mass spectrometry in the elemental analysis of agricultural soils. J Anal At Spectrom 28(12):1940–1948. https://doi.org/10.1039/c3ja50169h

- Jimu L, Mataruse L, Musemwa L, Nyakudya IW (2017) The miombo ecoregion up in smoke: the effect of tobacco curing. World Dev Perspect 5:44–46. https://doi. org/10.1016/j.wdp.2017.03.007
- Kowalska JB, Mazurek R, Gąsiorek M, Zaleski T (2018) Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination– A review. Environ Geochem Health 40(6):2395–2420. https://doi.org/10.1007/ s10653-018-0106-z
- Kozhevnikova AD, Seregin IV, Erlikh NT, Shevyreva TA, Andreev IM, Verweij R, Schat H (2014) Histidine-mediated xylem loading of zinc is a species-wide character in Noccaea caerulescens. New Phytol 203(2):508–519. https://doi. org/10.1111/nph.12816

Krämer U (2010) Metal hyperaccumulation in plants. Annu Rev Plant Biol 61:517– 534. https://doi.org/10.1146/annurev-arplant-042809-112156

- Kříbek B, Majer V, Veselovský F, Nyambe I (2010) 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 104(3):69–86. https://doi.org/10.1016/j. gexplo.2009.12.005
- Kříbek B, Nyambe I, Majer V, Knésl I, Mihaljevič M, Ettler V, Vaněk A, Penížek V, Sracek O (2019) Soil contamination near the Kabwe Pb-Zn smelter in Zambia: Environmental impacts and remediation measures proposal. *Journal of Geochemical Exploration*, 197(November 2018), 159–173. https://doi.org/10.1016/j. gexplo.2018.11.018
- Lee HK, Khaine I, Kwak MJ, Jang JH, Lee TY, Lee JK, Kim IR, Kim W, II, Oh KS, Woo SY (2017) The relationship between SO2 exposure and plant physiology: a mini review. Hortic Environ Biotechnol 58(6):523–529. https://doi.org/10.1007/s13580-017-0053-0
- Li MS, Yang SX (2008) Heavy metal contamination in soils and phytoaccumulation in a manganese mine Wasteland, South China. Air Soil and Water Research 1:31–41. https://doi.org/10.4137/aswr.s2041
- Li L, Wu H, Gestel CAM, Van, Peijnenburg WJGM, Allen HE (2014) Soil acidi fi cation increases metal extractability and bioavailability in old orchard soils of Northeast Jiaodong Peninsula in China. Environ Pollut 188:144–152. https:// doi.org/10.1016/j.envpol.2014.02.003
- Lin YF, Hassan Z, Talukdar S, Schat H, Aarts MGM (2016) Expression of the Znt1 zinc transporter from the metal hyperaccumulator noccaea caerulescens confers enhanced zinc and cadmium tolerance and accumulation to arabidopsis thaliana. PLoS ONE 11(3):1–30. https://doi.org/10.1371/journal.pone.0149750
- Lindahl J (2014) Environmental impacts of mining in Zambia: towards better environmental management and sustainable exploitation of mineral resources. Issue July. https://doi.org/10.1111/jicd.12105
- Lombi E, Tearall KL, Howarth JR, Zhao FJ, Hawkesford MJ, McGrath SP (2002) Influence of iron status on cadmium and zinc uptake by different ecotypes of the hyperaccumulator Thlaspi caerulescens. Plant Physiol 128(4):1359–1367. https://doi.org/10.1104/pp.010731
- Lotfi S, Chakit M, Belghyti D (2020) Groundwater quality and pollution index for heavy metals in Sais plain, Morocco. J Health Pollution 10(26):1–12. https:// doi.org/10.5696/2156-9614-10.26.200603
- Luo Z, Bin, He J, Polle A, Rennenberg H (2016) Heavy metal accumulation and signal transduction in herbaceous and woody plants: paving the way for enhancing phytoremediation efficiency. Biotechnol Adv 34(6):1131–1148. https://doi.org/10.1016/j.biotechadv.2016.07.003
- Mapani B, Ellmies R, Kamona F, Kříbek B, Majer V, Knésl I, Pašava J, Mufenda M, Mbingeneeko F (2010) Potential human health risks associated with historic ore processing at Berg Aukas, Grootfontein area, Namibia. J Afr Earth Sc 58(4):634–647. https://doi.org/10.1016/j.jafrearsci.2010.07.007
- Marcos DR, Jason P, Humberto G, Alba CA, Gustavo CJ, Alfredo C, Alberto DM, Jorge G-T (2011) Comparison of ICP-OES and XRF Performance for Pb and As Analysis in Environmental Soil Samples from Chihuahua City, Mexico
- Marguí E, Queralt I, Carvalho ML, Hidalgo M (2005) Comparison of EDXRF and ICP-OES after microwave digestion for element determination in plant specimens from an abandoned mining area. Anal Chim Acta 549(1–2):197–204. https:// doi.org/10.1016/j.aca.2005.06.035
- Matakala N, Chirwa PW, Mwamba TM, Syampungani S (2023) Heliyon Species richness and phytoremediation potential of mine wastelands-native trees across the zambian Copperbelt Region. Heliyon 9(3):e13585. https://doi. org/10.1016/j.heliyon.2023.e13585
- Mazurek R, Kowalska J, Gąsiorek M, Zadrożny P, Józefowska A, Zaleski T, Kępka W, Tymczuk M, Orłowska K (2017) Assessment of heavy metals contamination in surface layers of Roztocze National Park forest soils (SE Poland) by indices of pollution. Chemosphere 168:839–850. https://doi.org/10.1016/j. chemosphere.2016.10.126

Mihaljevič M, Jarošíková A, Ettler V, Vaněk A, Penížek V, Kříbek B, Chrastný V, Sracek O, Trubač J, Svoboda M, Nyambe I (2018) Copper isotopic record in soils and tree rings near a copper smelter, Copperbelt, Zambia. Sci Total Environ 621:9–17. https://doi.org/10.1016/j.scitotenv.2017.11.114

Millaleo R, Reyes-Díaz M, Ivanov AG, Mora ML, Alberdi M (2010) Manganese as essential and toxic element for plants: transport, accumulation and resistance mechanisms. J Soil Sci Plant Nutr 10(4):476–494. https://doi.org/10.4067/ s0718-95162010000200008

Milner MJ, Mitani-Ueno N, Yamaji N, Yokosho K, Craft E, Fei Z, Ebbs S, Clemencia Zambrano M, Ma JF, Kochian LV (2014) Root and shoot transcriptome analysis of two ecotypes of Noccaea caerulescens uncovers the role of NcNramp1 in cd hyperaccumulation. Plant J 78(3):398–410. https://doi.org/10.1111/ tpj.12480

Molnár V, Simon E, Ninsawat S, Tóthmérész B, Szabó S (2020) Pollution assessment based on element concentration of tree leaves and topsoil in ayutthaya province, Thailand. Int J Environ Res Public Health 17(14):1–13. https://doi. org/10.3390/ijerph17145165

Mondal S, Singh G (2022) Air pollution tolerance, anticipated performance, and metal accumulation capacity of common plant species for green belt development. Environ Sci Pollut Res 29(17):25507–25518. https://doi.org/10.1007/s11356-021-17716-8

Mulenga C (2022) Growth Response of Brachystegia longifolia to Copper Mining Pollution-Induced Heavy Metal Toxicity [Stellenbosch University]. https:// scholar.sun.ac.za/handle/10019.1/125906

Mulenga C, Clarke C, Meincken M (2020) Physiological and growth responses to pollutant-induced biochemical changes in plants: a review. Pollution 6(4):827–848. https://doi.org/10.22059/poll.2020.303151.821

Mulenga C, Clarke C, Meincken M (2022a) Bioaccumulation of Cu, Fe, Mn and Zn in native Brachystegia longifolia naturally growing in a copper mining environment of Mufulira, Zambia. Environ Monit Assess 194(1):1–13. https:// doi.org/10.1007/s10661-021-09656-0

Mulenga C, Clarke C, Meincken M (2022b) Growth response of Brachystegia Iongifolia to copper mining pollution-induced heavy metal stress. *International Journal of Environmental Science and Technology*, 0123456789. https://doi. org/10.1007/s13762-022-04310-9

Mzyk Z, Baranowska I, Mzyk J (2002) Research on grain size effect in XRF analysis of pelletized samples. X-Ray Spectrom 31(1):39–46. https://doi.org/10.1002/ xrs.534

Ncube E, Phiri B (2015) Concentrations of heavy metals in Eucalyptus and Pinus wood sawdust and smoke, Copperbelt province, Zambia. Maderas: Ciencia y Tecnologia 17(3):585–596. https://doi.org/10.4067/ S0718-221X2015005000052

Ngole-Jeme VM, Fantke P (2017) Ecological and human health risks associated with abandoned gold mine tailings contaminated soil. PLoS ONE 12(2). https://doi.org/10.1371/journal.pone.0172517

Nowrouzi M, Pourkhabbaz A (2015) Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Hara Biosphere Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Hara Biosphere. *Chemical Speciation & Bioavailability, 2299.* https://doi.org/10.3184/0954229 14X13951584546986

Nuchdang S, Niyomsat T, Pitiphatharabun S, Sukhummek B, Leelanupat O, Rattanaphra D (2018) Effect of grain size and moisture content on major and minor elements concentrations using portable X-ray fluorescence. *Journal of Physics: Conference Series*, *1144*(1). https://doi.org/10.1088/1742-6596/1144/1/012060

Olajire AA, Ayodele ET (2003) Study of atmospheric pollution levels by trace elements analysis of tree bark and leaves. Bull Chem Soc Ethiop 17(1):11–17. https://doi.org/10.4314/bcse.v17i1.61724

Olobatoke RY, Mathuthu M (2016) Heavy metal concentration in soil in the tailing dam vicinity of an old gold mine in Johannesburg, South Africa. Can J Soil Sci 96(3):299–304. https://doi.org/10.1139/cjss-2015-0081

Onjefu SA, Shaningwa F, Lusilao J, Abah J, Hess E, Kwaambwa HM (2020) Assessment of heavy metals pollution in sediment at the Omaruru River basin in Erongo region, Namibia. Environ Pollutants Bioavailab 32(1):187–193. https:// doi.org/10.1080/26395940.2020.1842251

Page V, Feller U (2015) Heavy Metals in Crop plants: transport and redistribution processes on the whole plant level. Agronomy 5(3):447–463. https://doi. org/10.3390/agronomy5030447

Page V, Weisskopf L, Feller U (2006) Heavy metals in white lupin: uptake, root-toshoot transfer and redistribution within the plant. New Phytol 171(2):329– 341. https://doi.org/10.1111/j.1469-8137.2006.01756.x Pietrelli L, Menegoni P, Papetti P (2022) Bioaccumulation of Heavy Metals by Herbaceous species grown in Urban and Rural Sites. Water Air Soil Pollut 233(4). https://doi.org/10.1007/s11270-022-05577-x

Ponette-González AG (2021) Accumulator, Transporter, substrate, and Reactor: multidimensional perspectives and approaches to the study of Bark. Front Forests Global Change 4(August):1–7. https://doi.org/10.3389/ ffgc.2021.716557

Radwan MA, Shumway JS, DeBell DS (1979) Effects of Manganese and Manganese-Nitrogen Applications on Growth and Nutrition of Douglas-fir Seedlings. *USDA* 

Reimann C, Arnoldussen A, Finne TE, Koller F, Nordgulen Ø, Englmaier P (2007) Element contents in mountain birch leaves, bark and wood under different anthropogenic and geogenic conditions. Appl Geochem 22(7):1549–1566. https://doi.org/10.1016/j.apgeochem.2007.03.048

Richau KH, Kozhevnikova AD, Seregin IV, Vooijs R, Koevoets PLM, Smith JAC, Ivanov VB, Schat H (2009) Chelation by histidine inhibits the vacuolar sequestration of nickel in roots of the hyperaccumulator Thlaspi caerulescens. New Phytol 183(1):106–116. https://doi.org/10.1111/j.1469-8137.2009.02826.x

Rietra RPJJ, Heinen M, Dimkpa CO, Bindraban PS, Rietra RPJJ, Heinen M, Dimkpa CO, Prem S (2017) Effects of nutrient antagonism and synergism on yield and fertilizer use Efficiency. Commun Soil Sci Plant Anal 48(16):1895–1920. https://doi.org/10.1080/00103624.2017.1407429

Rizvi A, Zaidi A, Ameen F, Ahmed B, Alkahtani MDF, Khan MS (2020) Heavy metal induced stress on wheat: phytotoxicity and microbiological management. RSC Adv 10(63):38379–38403. https://doi.org/10.1039/d0ra05610c

Roberts D, Nachtegaal M, Sparks DL (2005) Speciation of Metals in Soils. Chemical processes in soils. SSSA Book, pp 619–654. Soil Science Society of America. https://doi.org/10.1080/03067318408076997

Robin SL, Marchand C, Mathian M, Baudin F, Alfaro AC (2022) Distribution and bioaccumulation of trace metals in urban semi-arid mangrove ecosystems. Front Environ Sci 10(November):1–17. https://doi.org/10.3389/fenvs.2022.1054554

Rodríguez A, Guti C, Agraria T, Rodríguez Martin JA, Gutiérrez C, Torrijos M, Nanos N, Rodríguez A, Guti C, Agraria T (2018) Wood and bark of Pinus halepensis as archives of heavy metal pollution in the Mediterranean Region. Environ Pollut 239:438–447. https://doi.org/10.1016/j.envpol.2018.04.036

Roquette JG, Ortega-rodriguez DR, Portal-cahuana LA, Lobo FDA, Hevia A, Sánchez-Salguero R, Carvalho HWP, Tomazello-filho M (2023) Environmental forensics evaluation of residual soybean sludge using trees of brazilian savannah. Environ Nanatechnol Monit Manage 20(100814). https://doi. org/10.1016/j.enmm.2023.100814

Rouillon M, Taylor MP (2016) Can field portable X-ray fluorescence (pXRF) produce high quality data for application in environmental contamination research? Environ Pollut 214:255–264. https://doi.org/10.1016/j.envpol.2016.03.055

Sani I, Abdulhamid A, Bello F (2014) Eucalyptus camaldulensis: phytochemical composition of ethanolic and aqueous extracts of the leaves, stem-bark, root, fruits and seeds. J Sci Innovative Res 3(5):523–526. https://doi.org/10.31254/jsir.2014.3510

Schreck E, Foucault Y, Sarret G, Sobanska S, Cécillon L, Castrec-Rouelle M, Uzu G, Dumat C (2012) Metal and metalloid foliar uptake by various plant species exposed to atmospheric industrial fallout: mechanisms involved for lead. Sci Total Environ 427–428:253–262. https://doi.org/10.1016/j.scitotenv.2012.03.051

Schulz B (2010) Functional Classification of Plant Plasma Membrane Transporters. In A. S. Murphy, P. W., & S. B. (Eds.), *The Plant Plasma Membrane*. https://doi. org/10.1017/CBO9781107415324.004

Shaari NEM, Tajudin MTFM, Khandaker MM, Majrashi A, Alenazi MM, Abdullahi UA, Mohd KS (2024) Cadmium toxicity symptoms and uptake mechanism in plants: a review. Brazilian J Biology 84:1–17. https://doi. org/10.1590/1519-6984.252143

Shahid M, Schreck E, Xiong T, Khalid S, Niazi NK, Dumat C (2016) Foliar heavy metal uptake, toxicity and detoxification in plants: a comparison of foliar and root metal uptake. J Hazard Mater 325:36–58. https://doi.org/10.1016/j. jhazmat.2016.11.063

Sharma SS, Dietz KJ, Mimura T (2016) Vacuolar compartmentalization as indispensable component of heavy metal detoxification in plants. Plant Cell and Environment 39(5):1112–1126. https://doi.org/10.1111/pce.12706

Shen K, Zhang N, Yang X, Li Z, Zhang Y, Zhou T (2015) Dry ashing preparation of (quasi)solid samples for the determination of inorganic elements by atomic/ mass spectrometry. Appl Spectrosc Rev 50(4):304–331. https://doi.org/10.108 0/05704928.2014.986735

Shi X, Zhang X, Chen G, Chen Y, Wang L, Shan X (2011) Seedling growth and metal accumulation of selected woody species in copper and lead/

zinc mine tailings. J Environ Sci 23(2):266–274. https://doi.org/10.1016/ S1001-0742(10)60402-0

- Shi W, Zhang Y, Chen S, Polle A, Rennenberg H, Luo Z, Bin, Chen S, Polle A (2019) Physiological and molecular mechanisms of heavy metal accumulation in nonmycorrhizal versus mycorrhizal plants. Plant Cell Environ 42(4):1087–1103. https://doi.org/10.1111/pce.13471
- Singh AN, Singh JS (1999) Biomass, net primary production and impact of bamboo plantation on soil redevelopment in a dry tropical region. For Ecol Manag 119(1–3):195–207. https://doi.org/10.1016/S0378-1127(98)00523-4
- Storrs J (1995) Know your trees: some of the common trees found in Zambia. Regional Soil Conservation Unit, (RSCU)
- Sutherland RA (2000) Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ Geol 39(6):611–627. https://doi.org/10.1007/ s002540050473
- Tavares TR, Nunes LC, Alves EEN, de Almeida E, Maldaner LF, Krug FJ, de Carvalho HWP, Molin JP (2019) Simplifying sample preparation for soil fertility analysis by x-ray fluorescence spectrometry. Sens (Switzerland) 19(23):1–14. https:// doi.org/10.3390/s19235066
- Thanh-Nho N, Marchand C, Strady E, Huu-Phat N, Nhu-Trang TT (2019) Bioaccumulation of some trace elements in tropical mangrove plants and snails (can Gio, Vietnam). Environ Pollut 248:635–645. https://doi.org/10.1016/j. envpol.2019.02.041
- Tokaliog'lu Ş, Kartal Ş, Güneş AA (2001) Determination of heavy metals in soil extracts and plant tissues at around of a zinc smelter. Int J Environ Anal Chem 80(3):201–217. https://doi.org/10.1080/03067310108044370
- Tsuji T, Mambo A, Phiri LK, Msoni R, Sokotela SB, Yerokun OA (2005) Studies on nutrient distribution in some zambian soils with special reference to sulphur using GIS (Geographic Information Systems) II. Evaluation of plant-available sulphur and its distribution in major zambian soils. Soil Sci Plant Nutr 51(7):943–952. https://doi.org/10.1111/j.1747-0765.2005.tb00131.x
- Uddin MM, Cassim M, Zakeel M, Zavahir JS (2021) Heavy Metal Accumulation in Rice and aquatic plants used as. Toxics 9(360):1–19
- Väisänen A, Laatikainen P, Ilander A, Renvall S (2008) Determination of mineral and trace element concentrations in pine needles by ICP-OES: evaluation

of different sample pre-treatment methods. Int J Environ Anal Chem 88(14):1005–1016. https://doi.org/10.1080/03067310802308483

- Van Der Ent A, Vinya R, Erskine PD, Malaisse F, Przybyłowicz WJ, Barnabas AD, Harris HH, Mesjasz-Przybyłowicz J (2020) Elemental distribution and chemical speciation of copper and cobalt in three metallophytes from the copper-cobalt belt in Northern Zambia. Metallomics 12(5):682–701. https://doi.org/10.1039/ c9mt00263d
- White PJ (2012) Ion Uptake Mechanisms of Individual Cells and Roots: Short-Distance Transport. In *Marschner's Mineral Nutrition of Higher Plants* (p. 649)
- Yagura R, Imanishi J, Shibata S (2019) Effects of copper ions on the growth and photosynthetic activity of Scopelophila cataractae. Lindbergia 2019(1):1–7. https://doi.org/10.25227/linbg.01113
- Yang SX, Deng H, Li MS (2008) Manganese uptake and accumulation in a woody hyperaccumulator, Schima superba. Plant Soil and Environment 54(10):441– 446. https://doi.org/10.17221/401-pse
- Yang L, Li Y, Xj G, Ma X, Yan Q (2013) Comparison of dry ashing, wet ashing and microwave digestion for determination of trace elements in Periostracum Serpentis and Periostracum cicadae by ICP-AES. J Chil Chem Soc 58(3):1876– 1879. https://doi.org/10.4067/S0717-97072013000300018
- Zasoski RJI, Porada HJ, Ryan PJ, Gessep SP (1990) Observations of copper, zinc, iron and manganese status in western Washington forests. For Ecol Manag 37:7–25

ZEMA (2017) Zambia Environment Outlook Report 4

Zinkutė R, Radzevičius A, Taraškevičius R (2006) Ecological-Geochemical State of Topsoil and Water Sediments in Šiauliai. Environment. Technology. Resources. Proceedings of the International Scientific and Practical Conference, 1, 310. https://doi.org/10.17770/etr2003vol1.2026

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