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Influence of land use and topography on distribution and bioaccumulation of potentially toxic metals in soil and plant leaves: A case study from Sekhukhuneland, South Africa

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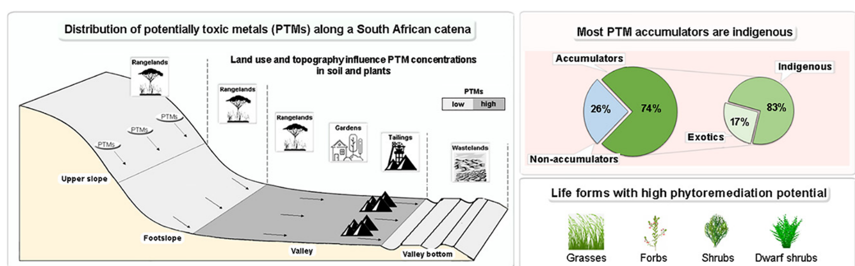
HIGHLIGHTS

- The surface soil throughout the investigated catena indicates Cr and Ni enrichment.
- Land use significantly influences the distribution of PTMs in soil and plant leaves.
- Most of the accumulators are indigenous species.
- Bioaccumulation of PTMs in leaf tissue is plant life form dependent.
- Leaves of most useful plants have Co and Cr levels above the permissible limits.

GRAPHICAL ABSTRACT



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ABSTRACT

Potentially toxic metal (PTM) enrichment of the soil-plant system in ultramafic and mining regions is a global concern as it affects the food chain. With expanding mining industry, it is important to assess if anthropogenic factors (i.e., land use practices) have a greater influence in this regard compared to natural factors (i.e., topography). Localities in Sekhukhuneland, South Africa, were selected along an altitudinal gradient (i.e., topography: upper slope, footslope, valley and valley bottom) and a land use profile (i.e., rangelands, gardens, tailings and wastelands) to investigate the distribution of Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Sr and Zn of natural (i.e., ultramafic geology) and anthropogenic (i.e., mining) origin in surface soil and plant leaf tissue. Plant life form was considered as an additional factor to evaluate PTM accumulation in leaves. Findings revealed a wider distribution range for Cr and Ni in the surface soil. Co, Cu, Mg, Mo, Sr and Zn were accumulated (bioaccumulation factor, BAF > 1) in leaf tissue of 74% of the evaluated plants of which 83% were indigenous. Grasses, forbs, dwarf shrubs and shrubs showed the highest accumulation levels. Despite an observed trend in the distribution of PTMs in soils and plant leaves along the altitudinal gradient, no significant differences were determined among the topographic positions. Land use practices, however, differed significantly indicating anthropogenic interference as a predominant determinant of PTM enrichment of soil-plant systems. Metal tolerant dominant plants in Sekhukhuneland could be classified as metallophytes. Indigenous species, accumulators and excluders, showed prospects for phytoremediation and rehabilitation of metal contaminated sites, respectively. Concentrations of Cr and Co in food and medicinal plant leaves exceeded the international permissible limits, which highlighted the necessity to estimate human health risks for PTMs in metalliferous sites.

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1. Introduction

Topography is the major determinant of the spatial distribution of elements in soils of a given area (Duan et al., 2015; Ding et al., 2017; Gaspar et al., 2020). Typically, soils generated from basaltic or ultramafic (e.g., serpentinite) outcrops are metalliferous with unusually high concentrations of potentially toxic metals (PTMs) (e.g., Co, Cr, Fe, Mg, Mn and Ni), low concentrations of essential plant nutrients (e.g., B, Ca, Mo, N and P) and a high Mg to Ca ratio (Brady et al., 2005; Rajakaruna and Boyd, 2014). Besides the predominant contribution from the parent material, the elemental composition of the surface soil further changes under the influence of weathering, erosion and sedimentation processes (Gaspar et al., 2020; Kierczak et al., 2021).

Anthropogenic factors such as land use further alter the quantity and types of PTMs within an edaphic system (Zhang et al., 2019). Mining activities, for instance, intensively modify existing soil properties by adding high quantities of multiple PTMs (Ding et al., 2017; Wang et al., 2019). Soil, in this case, acts as a sink for PTMs of both geogenic and anthropogenic origins (Wuana and Okieimen, 2011). In addition, soil erosion caused by vegetation clearing and overgrazing (Dlamini et al., 2011), or due to weak soil structure (Mirzabaev et al., 2016), can overtake the slow-paced pedogenesis process (Morgan, 2005), thereby, altering metal concentrations in the soil even further.

Metallophytes, plant species tolerant of metal-rich edaphic environments, comprise a considerable proportion of vegetation of ultramafic and mining areas, including the endemic taxa (Baker et al., 2010). Such plants require special attention since they can accumulate, hyperaccumulate or exclude abundant metals from soil (Baker, 1981; van der Ent et al., 2013; Siebert et al., 2018a). Species from metalliferous sites around the world are reported to hyperaccumulate PTMs such as Co (*Persicaria puncata*, van der Ent et al., 2020), Cu (*Geniosporum tenuiflorum*, Rajakaruna and Baker, 2004), Mn (*Macadamia neurophylla*, van der Ent et al., 2013), Ni (*Alyssum murale*, Drozdova et al., 2021; *Senecio conrathii*, Siebert et al., 2018a) and Zn (*Arabidopsis halleri*, Pollard et al., 2014).

Accumulators, hyperaccumulators and excluders are, therefore, valuable for green technologies applied in rehabilitation (i.e., re-vegetation to reclaim metal contaminated environments), restoration (i.e., re-establish the original vegetation in degraded ecosystems), phytoremediation (i.e., decontamination of polluted environments using plants) and phytomining (i.e., economically viable recovery of elements via hyperaccumulator plants) (Rajakaruna et al., 2006; Ali et al., 2013; O'Dell, 2014; Paul et al., 2018; van der Ent et al., 2015, 2021). Hence, PTM assessments of environmental matrices, such as soil along with their biota, may render essential information regarding suitable environmental management of areas prone to metal contamination (Gall et al., 2015; Marcelo-Silva and Christofoletti, 2019).

Globally, serpentine habitats with their unique floras, adapted to anomalous soil environments (Harrison and Rajakaruna, 2011), are threatened by factors such as climate change and human interference (Baker et al., 2010; Rajakaruna and Boyd, 2014; Mizuno and Kirihata, 2015), especially mining for metals as observed in South Africa (Williamson and Balkwill, 2006). In this study, Sekhukhuneland, in South Africa, was selected as a serpentine site featuring ultramafic outcrops of the eastern Rustenburg Layered Suite (RLS) (Scoon and Viljoen, 2019). The landscape of the study region is changing rapidly due to a shift in traditional land use patterns, primarily driven by the expanding mining industry and associated development (Quinn et al., 2011).

The north-south ranging Leolo Mountains in the study area provided a suitable catena to investigate the influence of topography and land use on the distribution of PTMs of natural (i.e., ultramafic soils) and anthropogenic (i.e., mining) origin in the soil-plant system. A catena is a succession of soils along a slope, with distinct soil characteristics due to variation in relief, altitude and removal and deposition of sediments (Malinowska and Szumacher, 2013; Schaetzl, 2013). Also, the area is well-known for its endemic flora with around 30 endemic and 50 near-endemic taxa adapted to ultramafic soils, for which it was recognized as a Centre of Plant Endemism (Van Wyk and Van Wyk, 1997; Siebert et al., 2001). Despite such plant diversity, the region is understudied in terms of identification of metallophytes that may present prospects for phytoremediation.

It was hypothesised that the topography and land use would have an influence on the PTM distribution in soils and above-ground plant parts along the catena in Sekhukhuneland, as reported for hilly regions (Tamfuh et al., 2017) and areas under the influence of human interference (Zhang et al., 2019). Also, it was predicted that the dominant plant species of the region could be classified as metallophytes (Baker, 1981) that exclude, accumulate or hyperaccumulate metals from the metal-rich soils as reported globally for ultramafic (Drozdova et al., 2021) and mining regions (Midhat et al., 2019). Furthermore, it was presumed that plant life form (i.e., habit) could be a determinant of metal accumulation in leaves as plants show typical morphological characteristics of serpentine-adapted species (Rajakaruna and Baker, 2004; Brady et al., 2005; Ernst, 2006) and certain life forms appear to be highly tolerant of the metalliferous soils of mine sites (Visoottiviseth et al., 2002; Paul et al., 2018). The specific study objectives were to (1) evaluate the influence of topography (i.e., a natural factor) and land use (i.e., an anthropogenic factor) on the distribution of the selected PTMs in surface soil and plant leaf tissue along the catena in Sekhukhuneland, (2) investigate foliar metal bioaccumulation potential of the dominant local plant species and estimate their phytoremediation potential, and (3) assess the influence of plant life form on the accumulation of the PTMs in leaf tissue.

2. Material and methods

2.1. Study area

The study area extends from 24°15′ S; 29°50′ E to 24°54′ S; 30°08′ E in the Sekhukhune district of the Limpopo Province in South Africa. Erosion of the eastern RLS of the Bushveld Igneous Complex formed the hilly physiography of the region with rugged mountain ranges and intermediate valleys. The ultramafic-mafic formation of the RLS is up to 10 km deep and around 30 km wide and was formed by multiple magma surges (Naldrett et al., 2012). The RLS is subdivided into five lithostratigraphic zones (i.e., rock layers; Fig. 1), of which the Critical Zone predominantly features chromitite rock layers of around 0.15 mm to > 2 m thick representing the largest global chromite reserve (chromite is the economically viable ore of chromium, Cr). These chromitite rocks further contain considerable proportions of platinum group metals (Scoon and Viljoen, 2019). Both Cr and platinum reserves of the eastern RLS are mined extensively in the study region.

The ultramafic soils derived from chromitite outcrops of the region are metal-rich and the associated vegetation is Sekhukhune mountain bushveld (Siebert et al., 2002). Semi-arid climatic conditions in the study area contribute to the edaphic profile of the catena, with shallow soil layers on the mountain slopes and deep alluvium in the valleys. Rainfall on slopes accelerates sheet erosion, culminating in gullies along the drainage lines, locally known as 'dongas', that causes severe soil displacement and degradation, especially in valley bottoms (valley bottom is the lowermost section of a landscape profile where slope decreases abruptly, Amare et al., 2019). Besides soil degradation by natural forces, existing communal lands and outcrops with their vegetation are threatened by intense mining, which contributes greatly to land use (15%) in the Limpopo province (Siebert et al., 2001; Quinn et al., 2011).

2.2. Site selection

Along a catena, the upper slope is characterized by constant outflux of matter, followed by a footslope which mainly determines mobilization and localized deposition, while valleys and valley bottoms primarily serve as landscapes for final deposition with severe erosion effects.

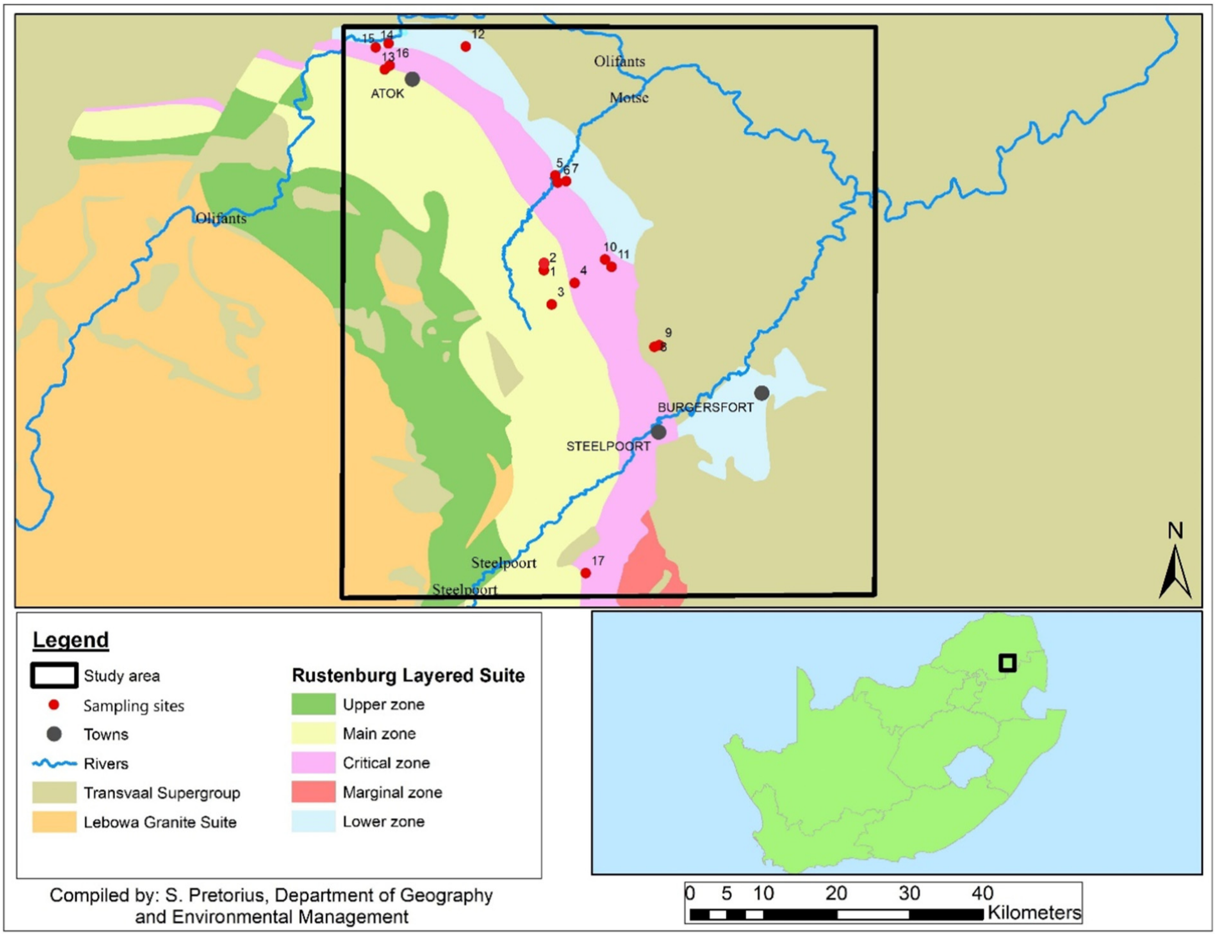

Fig. 1. Location of sampling sites along the Rustenburg Layered Suite in Sekhukhuneland, South Africa. The investigated catena decreases in altitude from west (984 m) to east (600 m).

Sampling sites were chosen randomly at various catena positions, starting from the upper slope to the valley bottom, targeting both less disturbed habitats as well as areas of mining activities and settlements, to assess the influence of topography along with human interference on the PTM distribution in soil and plants.

2.3. Sample collection

Soil and plant leaves were sampled during early summer (September-November 2018/2019) in Sekhukhuneland. A catena approach was selected and seventeen sites (Fig. 1) were investigated to assess PTM distribution in the soil and plant leaves sampled from the following topographic positions with specific land uses, (1) mountain slope (upper slope and footslope) with the land use: rangelands, (2) valley comprising three land uses: rangelands, gardens and tailing dams, and (3) valley bottom included the land use: wastelands of two types – sheet and gully erosion. Ten leaves from five individual plants were pooled in composite samples for each of the most abundant species at each site. The species were grouped according to their life forms: grasses, forbs (prostrate or erect; erect forms were subdivided into short (0.15–0.5 m) or tall (> 0.6 m)), dwarf shrubs, shrubs, succulents and trees.

After collection, leaves were washed three times with distilled water to remove surface debris. Thereafter, leaves were quickly washed with 0.1 M HCl solution followed by distilled water three times each, then air-dried and dehydrated in an oven at 35 °C for 48 h. Succulents were dried at 60 °C for 48 h. Surface soil (0.05 kg) from a depth of 0.1–0.15 m was randomly sampled four times at each sampling site, from the rhizosphere of sampled plants. The soil samples per site were mixed into a composite, air-dried and passed through a 2 mm sieve. Leaf and soil samples were ground in a tungsten carbide ring mill to a particle size < 75 μm and stored in labelled vials at room temperature until analysis.

2.4. Determination of total metals in soil and plant leaf tissue

An EPA 3051A microwave acid digestion method was applied. Each 200 mg of ground soil or plant sample (leaf dry weight) was placed in a Teflon tube and mixed with 9 ml of 65% nitric acid (HNO_3) and 3 ml of 32% hydrochloric acid (HCl) (HNO_3–HCl, 3:1, v/v). Sealed tubes were placed in a high-performance microwave digestion system (Milestone, Ethos UP, Maxi 44) for 20 min until the system reached 1800 MW and 200 °C. The state was maintained for 15 min, then tubes were cooled, and the final volume was adjusted to 50 ml. Soil and plant leaf samples were analyzed on an ICP-MS (Agilent 7500 series) to determine the total concentrations of Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Sr and Zn. For the purpose of quality assurance, the analysis of soil and plant samples were carried out in triplicate following the recommended precautionary measures for the ICP-MS.

2.5. Bioaccumulation factor (BAF)

The bioaccumulation factor (BAF) for each PTM was calculated to evaluate the foliar metal accumulation potential of the plant species, using the following equation (Midhat et al., 2019; Infante et al., 2021):

$$BAF = \frac{\text{Metal concentration in plant leaf tissue}}{\text{Metal concentration in soil}}$$

Plant species with BAF values > 1 were considered accumulators whereas species with values equal to or less than 1 were noted as indicators or excluders, respectively (Baker, 1981).

2.6. Statistical analyses

Data on PTM concentrations in soil and plant leaf samples did not follow normal distribution (Shapiro-Wilk's test, $p < 0.05$), and were therefore transformed (i.e., log (x + 1)) prior to analysis. This was also applied for a better scaling of the data together with an improved interpretation of the charts. Permutational multivariate analysis of variance (PERMANOVA) was applied to determine the influence of the topographic positions (i.e., natural factor), land uses (i.e., anthropogenic factor) and plant life forms (i.e., an additional factor for plants) on the PTM concentrations in sampled soils and plant leaves. The design for topography (i.e., 1 factor, 4 levels) was applied in samples from the upper slope (n = 4 for soil; n = 7 for plants), footslope (n = 3 for soil; n = 7 for plants), valley (n = 4 for soil; n = 7 for plants) and valley bottom (n = 8 for soil; n = 14 for plants). The land use design (i.e., 1 factor, 5 levels) was applied in samples from the rangelands (composed of samples from the upper slope, footslope and valley; n = 11 for soil; n = 21 for plants), gardens (n = 4 for soil; n = 7 for plants), tailings (n = 4 for soil; n = 7 for plants), sheet erosion (n = 4 for soil; n = 6 for plants) and gully erosion (n = 4 for soil; n = 7 for plants) – the last two being subsets of valley bottom. The life form design (i.e., 1 factor, 8 levels) was applied in samples of grasses (n = 4); dwarf shrubs (n = 6); shrubs (n = 6); succulents (n = 5); prostate forbs (n = 4); short, erect forbs (n = 7); tall, erect forbs (n = 7); and trees (n = 8). The selected PTMs, i.e., Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Sr and Zn were the variables within the three designs.

Further pairwise comparisons were conducted as a post hoc method (Anderson et al., 2008) to identify significant differences within each factor. Distance-based linear models (DistLM) were applied to identify the individual contribution of the PTMs to the distribution of the data in each of the three designs. Cluster analyses were performed to identify any possible grouping within the topographic positions, land uses and plant life forms. The resultant dendrograms were rendered from Euclidian distance matrices to depict the similarity among distances of the group averages. Statistical significance was considered at $p < 0.05$. Primer 6 and Permanova+ (PRIMER-E) were used for data analyses.

3. Results and discussion

3.1. PTM concentrations in surface soil

When total concentrations of the evaluated PTMs in the surface soils of the study area were compared with the Soil Screening Value 1 (SSV1, representing metal quantities safe for humans and ecosystems, considering all land uses) recommended by the Department of Environmental Affairs, South Africa (Appendix A, Table A.1), it was found that Ni concentrations exceeded the SSV1 for almost all sites across the catena. Cr, Cu and Mn levels exceeded such values for most tailing sites, while Cu and Mn levels in most of the sampled gardens were higher than the set SSV1. Co and Zn concentrations in all investigated sites were within the SSV1 levels. Cr and Ni levels also exceeded permissible levels recommended by the World Health Organisation (WHO) across the investigated catena. Co, Fe and Mn had concentrations greater than such limits in soils of tailing dams (Appendix A, Table A.1).

Cr, Cu, Mn and Ni enrichment of tailing and garden soils (located in rural areas in proximity to tailing facilities) may require remediation plans (Department of Environmental Affairs, 2012), Also, Cr and Ni concentrations exceeded the WHO levels (Chiroma et al., 2014; Nyika et al., 2019) throughout the catena soils, which indicate a greater distribution range for the two metals in both less disturbed (i.e., rangelands and wastelands) and highly disturbed (i.e., tailings and gardens) localities in Sekhukhuneland. Cr and Ni being important components of the RLS chromitite (Langa et al., 2021) may explain such occurrence.

Catena analyses, therefore, indicated variation in PTM concentrations in surface soils from different topographic positions with specialized land uses in Sekhukhuneland. Hence, both factors (i.e., topography and land use) should be evaluated to assess the distribution of PTMs in soil along a slope profile, as considered by Qiao et al. (2019). Further comparison of total metal concentrations with the reported metal levels in serpentine habitats worldwide (Mizuno and Kirihata, 2015; Williamson and Balkwill, 2015; Venter et al., 2018) confirms the ultramafic nature of the catena soils in Sekhukhuneland.

3.2. PTM concentrations in plant leaves

Out of the 47 evaluated species, 35 (74%) bioaccumulated (i.e., BAF > 1, based on mean dry weight) up to three of the PTMs, Co, Cu, Mg, Mo, Sr and Zn, in their leaf tissue (Appendix A, Table A.2; Fig. 2). Most accumulators (29 out of 35–83%) were indigenous. Accumulators included 60% of endemic (i.e., *Lydenburgia cassinoides*, *Euclea sekhukhuniensis* and *Polygala sekhukhuniensis*) and 60% of exotic (i.e., *Amaranthus spinosus*, *Argemone ochroleuca, Carica papaya*, *Ipomoea batatas*, *Moringa oleifera* and *Psidium guajava*) species. Comparatively higher BAF values for a maximum of three metals were determined for several indigenous species (including endemics) from rangelands and wastelands (i.e., *Aristida adscensionis*, *Blepharis pruinosa*, *Euclea linearis*, *Euclea sekhukhuniensis*, *Jamesbrittenia atropurpurea*, *Leucas capensis*, *Lydenburgia cassinoides*, *Orthosiphon fruticosus* and *Petalidium oblongifolium*) and tailings (i.e., *Cleome gynandra* and *Gomphocarpus fruticosus*) (Appendix A, Table A.2; Fig. 2). Exotic species, sampled only from tailings and gardens accumulated mostly Mo from both and Sr from tailing sites.

Although hyperaccumulation is common in serpentine floras (van der Ent et al., 2013, 2020; Siebert et al., 2018a), none of the species from the present investigation could be classified as such according to the criteria outlined by van der Ent et al. (2013). However, a trait for greater bioaccumulation by indigenous species adapted to metal-rich soils was observed (Siebert et al., 2018a, 2018b). Such species, with BAF values mostly > 1 for several PTMs might present better remediation potential than hyperaccumulators that generally remove single elements (Rajakaruna et al., 2006; Ferrero et al., 2020). Indigenous species are recommended to remediate metal contaminated mine soils (Visoottiviseth et al., 2002; Paul et al., 2018; Midhat et al., 2019). This is because they have desirable traits for phytoremediation, such as adaptation to local climate and edaphic conditions through fast growth rates and the ability to self-sustain in spite of metal accumulation (Muthusaravanan et al., 2018; Midhat et al., 2019).

Bioaccumulation was frequent in species from habitats with low disturbance, i.e., rangelands, especially in the upper slope and the footslope, and less common at the gardens and tailings, the highly disturbed habitats which had higher soil metal concentrations among all sites. This can be explained by the 'saturation effect,' according to which plants present greater metal uptake efficiency from soils with lower metal concentrations when compared to plants growing in soil with extremely high metal concentrations (Dudka and Miller, 1999).

Besides Mg, metals with the highest concentrations in soil, i.e., Cr, Fe, Mn and Ni were effectively excluded (BAF < 1) by all plant species. Species with high metal tolerance, but lacking hyperaccumulation as observed in the present study, is usually the norm. Such species have been reported for ultramafic areas in South Africa (Siebert et al., 2018b) and globally (Oze et al., 2008; van der Ent and Reeves, 2015), and mine sites and tailings (Mansfield et al., 2014; Paul et al., 2018; Midhat et al., 2019; Tang et al., 2021). Metal tolerant indigenous species, i.e., excluders should be investigated further to evaluate their

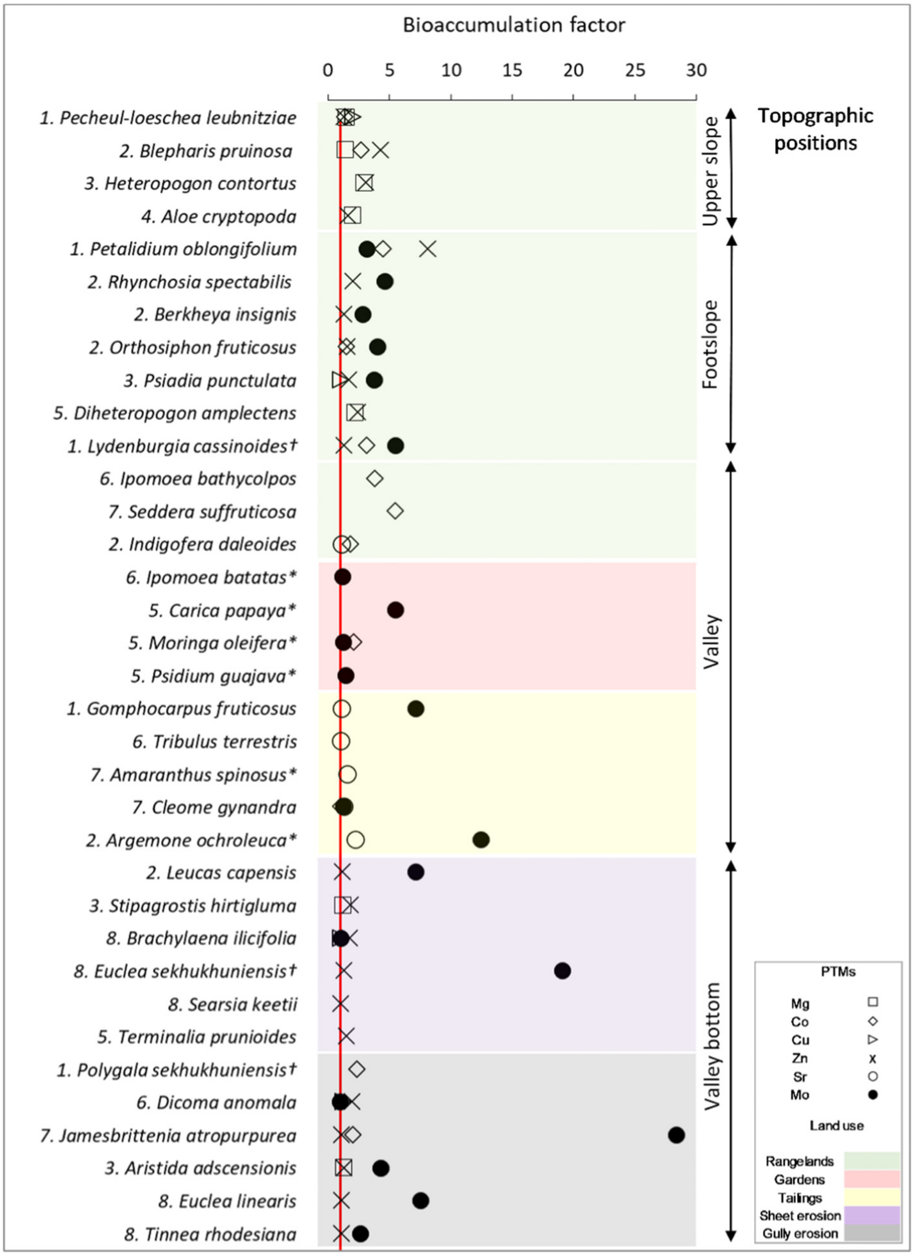

Fig. 2. Observed accumulators (BAF > 1 for 1 or more PTMs) across the investigated topographic positions (upper slope, footslope, valley and valley bottom) and land uses (rangelands, gardens, tailings and wastelands - sheet and gully erosion) in Sekhukhuneland. Plant life form: 1. dwarf shrub; 2. tall, erect forb; 3. grass; 4. succulent; 5. tree; 6. forb prostrate; 7. short, erect forb; 8. shrub. †Endemic and *exotic species. Red line indicates bioaccumulation threshold (BAF = 1). BAF, bioaccumulation factor. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

applicability to rehabilitate polluted mine sites in Sekhukhuneland (Paul et al., 2018; Midhat et al., 2019).

Dominant plants from Sekhukhuneland catena, therefore, differed in their response strategy to metalliferous soils, as some metals were accumulated in leaves while others were excluded. Soil parameters could have affected individual metal uptake mechanisms in the studied catena. For example, solubility of different oxidation states of Cr and Ni depends on pH, which ultimately influences their availability and uptake by plants (Oze et al., 2004; Wuana and Okieimen, 2011). Specifically for Cr, despite higher concentrations in soils of the study region, alkaline conditions could have restricted the availability and uptake of the most abundant oxidation state, Cr(III), which is highly stable at pH > 4 (Oze et al., 2004). Similarly, Mn availability and consequent uptake by plant species could be low in alkaline soils of Sekhukhuneland as Mn is more available at pH < 6 (Siebert et al., 2018b).

Therefore, dominant plants from Sekhukhuneland survive on soils enriched with both essential (i.e., Co, Fe, Mn and Ni) and non-essential (Cr) metals (Ernst, 2006). Thus, such species can be classified as metallophytes (Baker et al., 2010; Boyd and Rajakaruna, 2013; Pollard et al., 2014). Differential uptake, translocation and accumulation mechanisms for individual metals are consequence of the evolution of metal tolerance in metallophytes, to limit the detrimental effects of metals on physiological processes (Brady et al., 2005; Ernst, 2006; Baker et al., 2010), as can be suggested for metallophytes from Sekhukhueland. Advances in the study of metal tolerance mechanisms of metallophytes, especially the use of genetically modified plant species must be pursued since they improve the prospects for phytoremediation (Ali et al., 2013; Muthusaravanan et al., 2018). In this sense, further research on metal tolerant genotypes in Sekhukhuneland may help identify species most suitable for remediation of polluted sites.

3.2.1. PTM distribution among plant life forms

Cluster analysis based on group averages of PTM concentrations in leaf tissue arranged grasses and shrubs as two extreme groups in the dendrogram (Fig. 3a). The remaining life forms were placed in the between, with short forbs being similar to shrubs. Such grouping was confirmed by the pair-wise analysis, which indicated significant differences between shrubs and grasses and the two from the rest of the life forms (Appendix A, Tables A.3 and A.4). From this, it seems that sampled grasses and shrubs have distinct foliar metal accumulation patterns from the other life forms. DistLM analysis indicated Co (35% of contribution), Cr (22%) and Mg (14%) as the main metals driving the variation in life form data (Appendix A, Table A.5). Only Co levels differed significantly among the life forms, with the lowest concentrations in grasses (Fig. 3b).

Most of the 35 accumulators were tall, erect forbs (7 species), followed by dwarf shrubs, shrubs and trees (5 species each), grasses, prostate and short forbs (4 species each), and lastly, 1 succulent species. Out of the six accumulated PTMs, only Zn was accumulated by all sampled grass species and at least one species within each of the observed life forms. Grasses had the highest proportion of species accumulating most of the PTMs (Fig. 4). Dwarf shrubs accumulated all six PTMs, while a low percentage of succulent species accumulated only Mg and Zn (Fig. 4).

The overall difference in concentrations of PTMs in leaves of the grasses, shrubs and other life forms reflected how plant life form can also be a predictor of metal accumulation. Grasses in our study excluded Co as similarly reported by Oze et al. (2008), but accumulated several other PTMs. Our findings contradict the well-documented metal tolerance of grasses on both natural and anthropogenic metalliferous soils

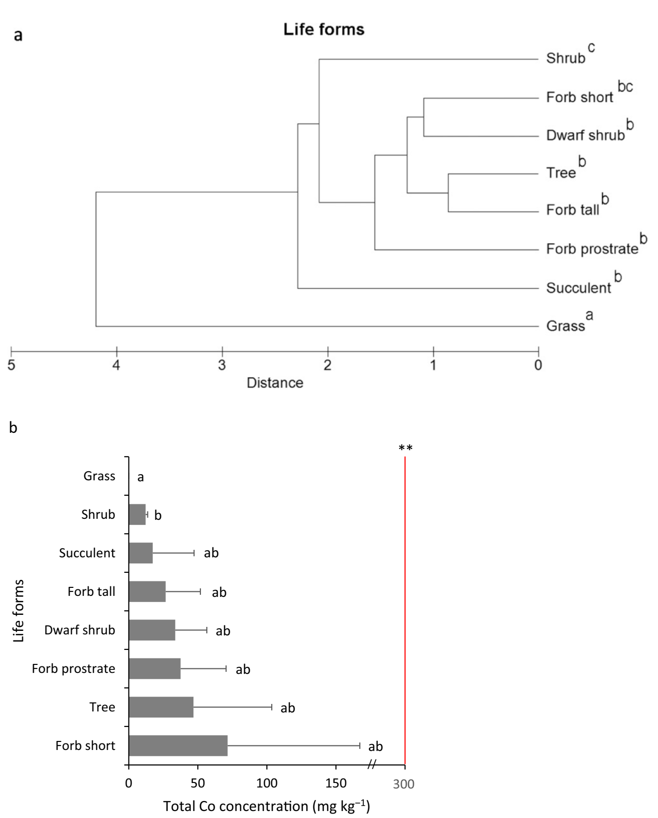

Fig. 3. a. Dendrogram of PTM distribution ordination of plant life forms based on group averages of PTM concentrations. Pairwise post hoc comparison results are added to the dendrogram to show significant differences among life forms. Different letters represent significant difference ($p < 0.05$). b. Total Co concentrations among life forms. **Red line indicates hyperaccumulation threshold (van der Ent et al., 2013). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

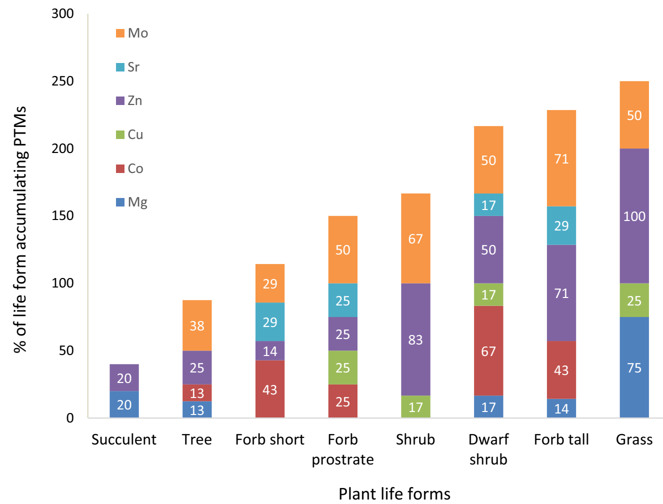

Fig. 4. Accumulators among plant life forms, according to six accumulated PTMs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

by limiting metal translocation from root to shoot (Ernst, 2006; Oze et al., 2008; Paul et al., 2018). Hence, grasses should be investigated further in the study region.

Besides Co, noteworthy differences among life forms regarding foliar Cr concentrations can be related to the tolerance of serpentine plants to geogenic Cr (Oze et al., 2008), but in general, Cr uptake is enhanced with an increase in Cr level in growth media (Wakeel and Xu, 2020), as observed in polluted mining localities in Sekhukhuneland. Serpentine plants show preferential uptake of Mg for optimal growth (Brady et al., 2005), which may explain found variations in foliar Mg levels in dominant plant species from Sekhukhuneland.

Except for Co, the present study did not point out any other metals to be accumulated more or less effectively by particular life forms. Nevertheless, accumulation of multiple PTMs altogether could be differentiated among life forms. Future investigations should focus on grasses, forbs, shrubs and dwarf shrubs to identify the best-fit species to be considered for phytoremediation in Sekhukhuneland. Indigenous grasses, shrubs and forbs have been identified as metallophytes suitable for phytoremediation and rehabilitation of contaminated mine sites (Visoottiviseth et al., 2002; Paul et al., 2018; Tang et al., 2021).

3.3. Patterns of PTM distribution

3.3.1. Natural factor – topography

PERMANOVA results showed no significant differences among the topographic positions regarding PTM levels in soil and plant leaves (Appendix A, Table A.6). There was, however, a trend of similar grouping patterns for soils and plant leaves as revealed by the metal distribution ordinations (Fig. 5). In the dendrograms, the upper slope and the valley samples formed separate groups for soils and plant leaves, respectively. Soils sampled from upper slope localities and plant leaves collected from valleys tend to exhibit distinct PTM concentrations compared to other topographic positions (i.e., footslope and valley bottom). Additional DistLM analysis indicated Ni (51% of contribution), Mg (17%) and Mo (13%) as the main PTMs driving such distribution within soil. While for plants, Co (33%), Fe (26%) and Mg (13%) were the main metals contributing to the distribution within the plant material (Appendix A, Table A.5).

The trend for distinct PTM concentration in soils of the upper slopes could be a reflection of the parent material mineralogy (Gaspar et al., 2020), which usually have higher quantities of metals (Qiao et al., 2019) compared to the other slope positions. However, soils on the

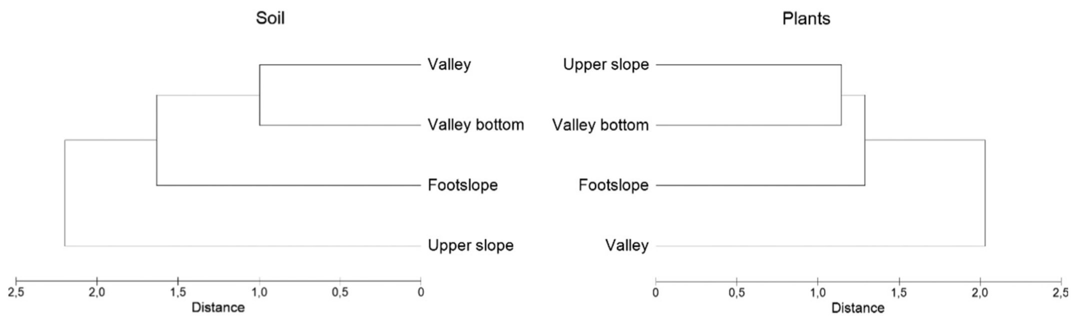

Fig. 5. Dendrograms of PTM concentration ordinations of the soil and plant leaf samples based on group averages of PTM concentrations under the topographic factor.

upper slopes are shallow (Duan et al., 2015; Ding et al., 2017; Qiao et al., 2019) and can be eroded easily by natural factors such as gravity, water and wind, resulting in loss of metals from the surface soil (Duan et al., 2015; Tamfuh et al., 2017). Such erosion effects are prominent in sloping serpentine outcrops with rocky soil structures that lack clay and moisture to bind the soil (Brady et al., 2005) as observed in Sekhukhuneland.

For plant leaves, the distinct metal distribution trend observed for the valley could be attributed to higher availability of metals trapped in soils rich in clay content (Alloway, 2013) as reported for the study region (Siebert et al., 2002). In valleys, greater deposition of eroded metals from mountains and waterways is in contrast with the upper slope and valley bottom, which are primarily characterized by displacement of surface soil (Duan et al., 2015; Tamfuh et al., 2017; Du Plessis et al., 2020) and fast leaching of the metals. Tamfuh et al. (2017) also reported variations among slope positions regarding mobility and distribution of individual elements in soil and plants.

In our study, distinct differences in Mg, Mo and Ni levels in soil along the altitudinal gradient validate typical abundance (i.e., Mg and Ni) or scarcity (Mo) of metals in ultramafic soils worldwide (Rajakaruna and Baker, 2004; Kierczak et al., 2021). On the other hand, serpentine plants are tolerant of higher availability of Co, Fe and Mg in soils, but can also accumulate these metals and survive (Brady et al., 2005; Mizuno and Kirihata, 2015; Siebert et al., 2018b; Drozdova et al., 2021). This might explain the found variation in distribution of these three metals in leaves of plant species in the present study.

3.3.2. Anthropogenic factor – land use

Cluster analysis grouped tailings separately from other land uses for soil samples, while for plants, tailings and gardens were clustered as a distinct group than the rest of the land uses (Fig. 6). This trend was reflected by pairwise comparisons, where tailings and gardens differed significantly from the rangelands and wastelands regarding PTM levels in soils and plants (Appendix A, Tables A.6 and A.7; Fig. 6). Selected analyses differentiated highly disturbed sites (i.e., tailings and gardens) from comparatively less disturbed localities (i.e., rangelands and wastelands) in terms of PTM distribution in soil and plant samples. DistLM analyses indicated Cr (77% of contribution), Sr (8%) and Mg (6%) as the metals driving the variation among the soil data. Cr was determined as the only metal that had significantly higher levels in tailing soils compared to other land uses (Fig. 7). Co (35%), Cr (22%) and Mg (14%) were identified as the major metals to drive variation in plant data (Appendix A, Table A.5).

Comparatively higher PTM concentrations in soil and plant leaves sampled from tailings and gardens in the present study exemplify the greater influence of anthropogenic interference on PTM enrichment of the soil-plant system in a mine site as also discussed by Mansfield et al. (2014). Chromium mine tailings contain considerably higher proportions of Cr and other metals such as Fe, Mg, Mn and Ni (Dhal et al., 2010; Özgen, 2012), which further supports our findings. High bioavailability of metals is often the case for tailing soils (Paul et al., 2018) as could be verified for Sekhukhuneland, resulting in greater concentrations of PTMs in plant leaves.

As noted by Dhal et al. (2010) and Wang et al. (2019), leachate from Cr and other metal mine tailings, in general, contains high concentrations of several PTMs that pollute surrounding areas. Such can also be stated for gardens located in the vicinity of tailings in Sekhukhuneland as proximity to polluters enhances the contamination possibility of soil and vegetation (Zhang et al., 2019). Metal enrichment in garden soils and crops around mines and tailings has been reported globally (Alloway, 2013; Antisari et al., 2020). Considering the historical reliance of the rural populations on home garden grown crops (Lubbe et al., 2011; Mogale et al., 2019), gardens in Sekhukhuneland should be investigated further for PTM contamination of the soil-plant systems.

Differences between the less disturbed (i.e., rangelands and wastelands) and disturbed (i.e., gardens and tailings) areas in Sekhukhuneland in terms of PTM levels in soil and plant materials, could firstly be due to slow release of metals from geogenic sourced minerals that are less available (Oze et al., 2004; Wuana and Okieimen, 2011). Furthermore, overgrazing common in rangelands of Sekhukhuneland could be an additional agent to induce and aggravate soil erosion, especially in wastelands (i.e., gully and sheet erosion sites) in hilly regions (Dlamini et al., 2011; Alfonso-Torreño et al., 2021) leading to metal loss.

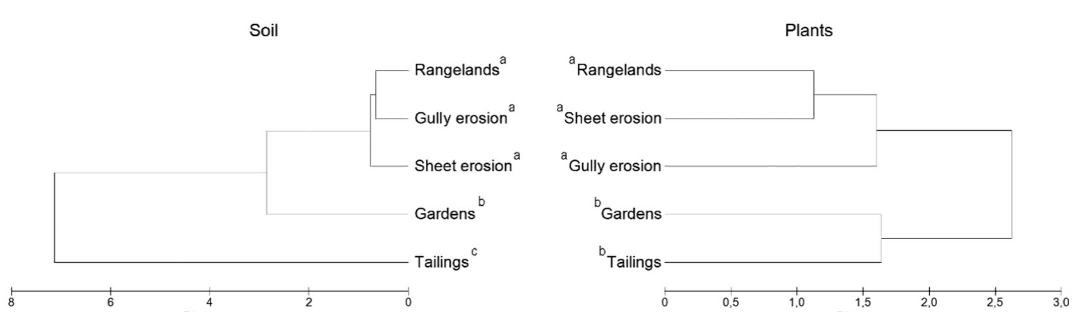

Fig. 6. Dendrograms of PTM concentration ordinations of the soil and plant leaf samples based on group averages of PTM concentrations under the land use factor. Pairwise post hoc comparison results are added to the dendrograms to show significant differences among the investigated sites. Different letters indicate significant difference ($p < 0.05$).

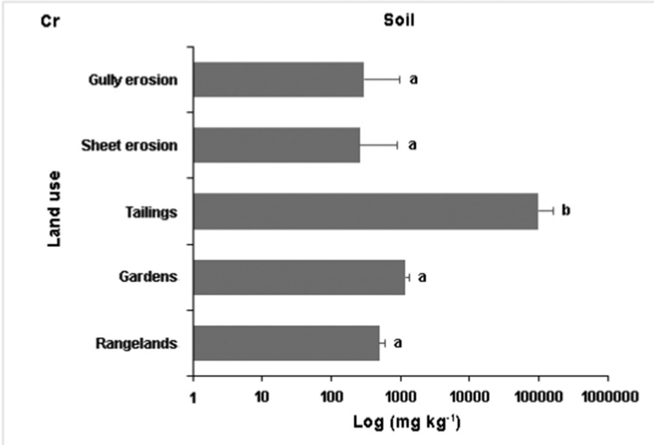

Fig. 7. Total Cr concentration in surface soil under the land use factor. Different letters represent significant difference in the pairwise post hoc comparison ($p < 0.05$).

Cr contributed most to the soil metal variations among the land uses evaluated in this study. This suggests that although Cr is a major natural component of ultramafic outcrops in Sekhukhuneland (Siebert et al., 2002), mining operations exacerbate soil contamination. Mg and Sr, the other main elements with considerable concentration variations in soil, are the characteristic components of the RLS geochemistry related to the origin of chromitite (Naldrett et al., 2012). Greater concentration variation of Co in plant leaves could be explained by the fact that Co is one of the most associated metals with chromite (Alloway, 2013) and mining could have increased Co availability to plants even further. In addition, Cr and Mg, as major constituents of serpentine soils and chromite ore explain their concentration variations in leaf tissue. Hence, in the study region, Co, Cr, and Mg affect the metal-plant relationships in land uses characterized by both less disturbed chomitite outcrops and intense mining.

The similarity in the distribution of metals in both soil and plant samples, under the evaluated natural (i.e., topography) and anthropogenic (i.e., land use) factors in this study, provide evidence for the fact that both factors influence metal concentrations in the catena. Moreover, considering the mining history, a greater influence of the land use factor on metal-soil-plant system was expected for the study region. Therefore, Sekhukhuneland is characterized by features of 'secondary metalliferous sites' where outcrops are exploited extensively by mines, creating an ideal habitat for metallophytes (Baker et al., 2010).

Often, concentrations of metals in plant parts are affected by the available fractions of the corresponding metals in ultramafic soils (Drozdova et al., 2021). Also, metal tolerance and distribution of plant species depend on the bioavailability of metals in soil (Ernst, 2006; Paul et al., 2018). Therefore, further investigation on PTM bioavailability in catena soils may improve the understanding of soil-plant interactions in Sekhukhuneland. For soil, evaluation of both total and soluble fractions of PTMs is crucial to comprehend the contamination levels (Qiao et al., 2019).

3.4. PTM concentrations in food and medicinal plant leaves

The 47 plants investigated in this study, included 14 species (~30%) with recorded food and/or medicinal use of leaves in Sekhukhuneland (Appendix A, Table A.2). Most of the useful plants (12 out of 14–86%) were sampled from disturbed habitats (i.e., tailings and gardens). Among the 10 analyzed PTMs, foliar concentrations (based on mean dry weight) of only Co and Cr exceeded corresponding maximum permissible levels suggested by WHO and Food and Agriculture Organization (FAO) (Appendix A, Table A.2). Foliar Cr concentrations exceeded such limit (2.3 mg kg^{-1}) in all assessed food/medicinal species, being 22 times above the limit in *Argemone ochroleuca* (51.5 mg kg^{-1}). Co concentrations were above such limit (50 mg kg^{-1}) in 6 out of 14 species and around 5-fold higher concentration was observed in *Cleome gynandra* (271.1 mg kg^{-1}).

Cr and Co concentrations above the WHO/FAO permissible levels (Chary et al., 2008; Pajević et al., 2018) was expected based on elevated quantities and availability of these toxic metals in ultramafic and mining affected soils (Dhal et al., 2010; Kierczak et al., 2021). Although foliar concentrations of the remaining PTMs mostly stayed within the permissible levels (Mensah et al., 2009; Ametepey et al., 2018), it is recommended that all PTMs should be assessed for human health risks in Sekhukhuneland, given their possible adverse effects on human health (Ali et al., 2013; Kierczak et al., 2021). Also, elevated human health risks were reported for exposure to multiple hazardous elements via consumption of useful crops harvested from mining regions (Antisari et al., 2020; Wang et al., 2021). In Sekhukhuneland, a greater number of plant species from less disturbed outcrops should be evaluated for PTM linked health risks as often predicted for ultramafic regions (Infante et al., 2021; Kierczak et al., 2021).

Adhikari et al. (2021) reported Cr dust deposition on unwashed leaf surfaces of some of the same food and medicinal plant species sampled from the same catena of this study. Hence, despite careful washing of the leaf materials in this study, remains of deposited metalliferous dust particles could have influenced the data, as also pointed out by Paul et al. (2018) for a mining locality in Australia. The same authors suggested controlled greenhouse experiments are necessary for further confirmation.

4. Conclusions

The study unravelled the influence of topography and land use on the distribution of PTMs in the soil-plant system along a catena in Sekhukhuneland and indicated foliar accumulation potential of several dominant plant species. Cr and Ni enrichment throughout the catena soil suggests a relatively wider distribution range for these two PTMs. Compared to topography, a greater influence of land use on PTM enrichment of soils and plant leaves suggests human interference as a principal driver in this regard. Cu, Mn and Ni enrichment and significantly higher Cr levels in tailing soils indicate a need for remediation considering the high density of settlements around mines in Sekhukhuneland.

Dominant indigenous (including endemic) and exotic plant species from Sekhukhuneland could be classified as metallophytes that survive on metalliferous soils by accumulating Co, Cu, Mg, Mo, Sr and Zn and excluding Cr, Fe, Mn and Ni. Although none of the metallophytes could be identified as hyperaccumulators, several indigenous species from both natural and disturbed habitats showed greater bioaccumulation abilities for 2-3 PTMs and might be considered to remediate metal contaminated sites. On the other hand, excluders could be used to rehabilitate mine sites, especially to restrict soil erosion. Remediation abilities of indigenous grasses, forbs, dwarf shrubs and shrubs should be explored further. Hence, future research on metallophytes of the region should be prioritized to identify the best-performing species suitable for green technologies.

It is important to conduct human health risk assessments for PTMs in ultramafic and mine regions to ensure the safe use of locally harvested plant materials. Globally, continuous monitoring of the spatial distribution of hazardous metals in soils is urgent, specifically in metalliferous sites, as rapidly changing land use patterns could lead to further alterations in metal-soil-plant dynamics at the landscape level, which ultimately influence the food chain.

CRediT authorship contribution statement

S. Adhikari Conceptualization, Resources, Writing - Original draft preparation, review and editing. **J. Marcelo-Silva** Statistical analyses, Supervision, Writing - Original draft preparation, review and editing. **N. Rajakaruna** Resources, Writing - review and editing. **S.J. Siebert**

Conceptualization, Data curation, Methodology, Resources, Supervision, Writing - Original draft preparation, review and editing. All authors reviewed and amended the original manuscript and subsequent revised versions.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.150659.

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