Metal Accumulation of Plants in a Nickel Laterite Mine and Their Phytoremediation and Phytomining Potential

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Metal Accumulation of plants in a nickel laterite mine and their phytoremediation and phytomining potential

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Abstract: *Phytoremediation is an environment-friendly technique that uses plants to extract contaminants like metals from soil. This has found application in waste management and possibly in future mining through phytomining. This study wanted to evaluate the metal accumulation of plants, thriving in a nickel laterite mine for Cr, Mn, Ni, Cu, and Zn and determine their potential for phytoremediation or phytomining. The metal accumulation in crops is also highlighted for their possible harmful effects to humans. Samples of soil, roots, stems, leaves, and fruits were gathered. The plants were evaluated based on their metal accumulation in the above-ground part, leaf-to-root ratio, bioaccumulation coefficient (BAC), and translocation factor (TF). The plant Leucaena leucocephala, Pennisetum polystachion, Casuarina cunninghamiana, and Mimosa pudica shows significant accumulation. The crops showed substantial amounts of metal which can be harmful to humans. The planting of hyperaccumulator plants is recommended for future phytomining application but planting crops is highly discouraged due to possible accumulation of metals which can be harmful for humans.*

Keywords: Nickel laterite, Mine waste, Waste management, Phytoremediation, Phytomining

1. INTRODUCTION

Nickel laterite mines are usually left with substantial amount of low-grade soil, silt, dust, and other wastes after mining [1]. If not managed properly, these wastes could cause environmental issues like water turbidity, siltation, and dust problems. The waste contains some metals, which are currently too low for economic extraction but too high if discharged to water and neighboring agricultural land. The current and widely used rehabilitation technique is revegetation, using plant species that are known to withstand the challenging environmental conditions in a mine. There are other ways that the mined-out area can be utilized, which include further extraction of waste using metallurgical process, bio-mining, production of ceramic and polymers, use of the mined-out area for solar or wind farm, or extraction of metals using plants, or phytomining [2].

Phytomining, is a technique using hyperaccumulator plants that can remove the metals from the soil and simultaneously contribute to energy production through biomass energy [3–5]. To be qualified for phytomining, plants must be hyperaccumulators of the metal, have high biomass, and be easily regenerated [6]. Phytomining relates to phytoremediation, wherein metals are extracted from soil using plants. Conversely, phytoremediation is an environment-friendly technique for cleaning contaminated areas. Phytoremediation has found its application in waste management, both in solid and water waste [7,8]. However, the problem with phytoremediation alone is the accumulation of metal in plants and their disposal, which will eventually return to the soil if not appropriately treated. With this, phytoremediation efforts must be coiled with phytomining to ensure the extracted metals are utilized. The major difference between them is the economic consideration in phytomining which is highly affected by metal prices, and cost of processing.

Accumulation of metals is a way for plants to adapt in metalliferous soil, like in a mine site [9]. Although metals have essential roles in plant growth, they also have some hazardous effects on plants in high amounts [10]. Nickel, for example, is known to be essential for metabolic activities in plants, but in excess, it can also reduce shoot and root growth, cause poor development of branches, cause abnormal flower shape, and cause other plant abnormalities [11,12]. These abnormalities could eventually lead to reduced crop yield [11].

In this study, plants found in the mined-out areas of the mine are chosen because they are already known to withstand the condition in the mine, and thus, they will be easy to grow and reproduce. The plants are analyzed for their nickel, copper, zinc, manganese, and chromium content and evaluated if they can be considered hyperaccumulators. If a plant is a hyperaccumulator, it can be propagated and used for mine rehabilitation, possibly for phytomining or other waste management applications such as treating metal-contaminated landfills. The plants are evaluated for hyperaccumulation using the amount of heavy metal accumulation (HMA) in the above-ground portion of the plant [13–15], the leaf-to-root (L/R) ratio [9], bioaccumulation coefficient (BAC) [8,16], and Translocation Factor (TF) [8,16].

The crops are also evaluated for their accumulation in the edible part of the plants. Many mines in the Philippines consider planting crops as an alternative land use after mining. The mine workers and people in the community usually consume the harvests. The metal accumulation in crops in the mined-out areas is analyzed for their implications on human health.

2. METHODOLOGY

This study is conducted in a nickel laterite mine in the Philippines. Three samples of each endemic and grown plant species were taken randomly around the mine where there is already vegetation. Samples of the soil, roots, stem, leaves, and flowers or fruits (if available) were taken for metal content analysis using X-ray fluorescence (XRF). The soil samples were dried directly in an oven at 105°C until completely dried. The roots, stem, leaves, and flowers or fruits (if available) were washed thoroughly with running water and initially sun-dried in an elevated space to ensure no dust contamination. After sun drying of the plants, the samples were oven-dried at 80°C to avoid loss of volatile substances (15). Samples were then crushed using mortar and pestle into smaller bits to fit the sample holder for XRF analysis.

2.1 Evaluation and Analysis

The first method used in the evaluation is the heavy metal accumulation. The threshold to be considered hyperaccumulator is in Table I. The threshold for Cu is 300 mg/kg, Cr and Ni is 1,000 mg/kg, Mn is 10,000 mg/kg, and 3,000 mg/kg for Zn.

Table 1. Metal accumulation threshold for hyperaccumulator plants

Metal	Hyperaccumulation Threshold (mg/kg)	Reference
Cu	300	Van der Ent *et al*.(14)
Cr,Ni	1,000	Baker and Brooks (13)
Mn	10,000	Baker and Brooks (13)
Zn	3000	Van der Ent et al.(14)

Another method used to evaluate hyperaccumulation is the leaf-to-root ratio (9), which is the ratio of the amount of metals in the leaf to the amount of metals found in the roots. According to Baker (1981), the L/R of > 1 is a characteristic of an accumulator, while L/R of < 1 is of an excluder (9). Accumulator plants transport the metal to the leaves, while excluder plants tend to restrict the transport (9) and accumulate the metals in the roots.

The Bioaccumulation coefficient (BAC), and Translocation factor (TF) is another method to evaluate hyperaccumulator plants. Their values must be > 1 (8,13,15). BAC and TF are calculated as follows (8,13):

$$BAC = \frac{C_{shoot}(mg/kg)}{C_{soil}(mg/kg)} \qquad (1)$$

$$TF = \frac{C_{shoot}(mg/kg)}{C_{roots}(mg/kg)} \qquad (2)$$

where:

$C_{roots} =$ *is the concentration of metal in the roots in mg/kg*

$C_{soil} =$ *is the concentration of metal in the soil in mg/kg*

$C_{shoot} =$ *is the concentration of metal in the above ground portion of the plant in mg/kg*

The significance of the results is evaluated using the one-sided t-test in SPSS software. The t-test compares the mean values of the experimental results with those generally accepted to be considered hyperaccumulator plants. The p-value is set at 0.05, meaning that if p-value is 0.05 or lesser, the experimental results have no significant difference or are significantly higher than the test value. The test value for HMA is in Table 1, which is 300mg/kg for Cr and Cu, 1,000mg/kg for Ni, 3,000mg/kg for Zn and 10,000 mg/kg for Mn. The leaf-to-root ratio, BAC, and TF test value is 1 (8,13,15). All plants with p values $\leq$ 0.05 are considered significant hyperaccumulators.

Based on available literature or previous studies, significant hyperaccumulators are further investigated for their biomass or bioenergy. The plants are already known to survive the challenging environment of the mine, so their propagation may not be a problem.

3. RESULTS AND DISCUSSION

3.1 Identification of hyperaccumulator plants by evaluating the metal accumulation in the above ground parts of the plants

The average accumulation in the aboveground portion (stem and leaves) of plants for chromium is in Fig. 1. *Mimosa pudica, Pennisetum polystachion,* and *Colocasia esculenta* shows mean accumulation for chromium above 1,000 ppm. However, only *Mimosa pudica* is significant with $p < 0.05$ using t-test.

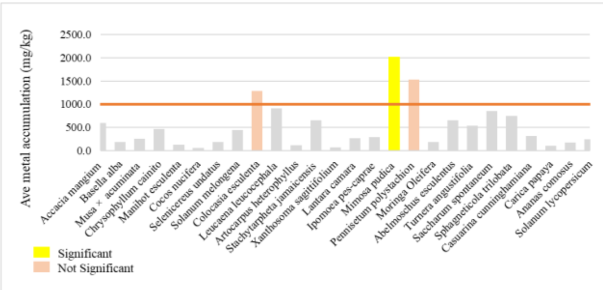

Fig. **1.** Cr metal accumulation in plants

For nickel, the above ground HMA is in Fig. 2. *Leucaena leucocephala, Mimosa pudica, Pennisetum polystachion,* and *Chrysophyllum caimito* are found to accumulate the metal significantly. *Accacia mangium* and *Saccharum spontaneum* are potential hyperaccumulators.

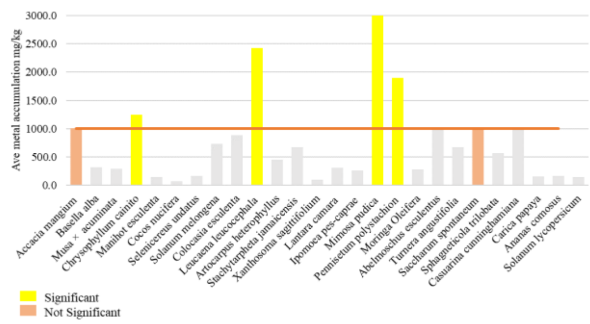

Fig. 2. Ni metal accumulation in plants

For Mn, Cu, and Zn the metal content of all the plants are below the threshold. However, it is noted that the metal content of the soil is lower than the threshold of 300mg/kg for Cu, 3,000mg/kg for Zn, and 10,000mg/kg for Mn.

3.2 Identification of hyperaccumulators by Leaf/ Root (L/R) Ratio

According to Baker (1981), there can be three types of relationship between metal in plants and metal in soil namely; accumulator, indicator, and excluder. Accordingly, the L/R ratio of >1 is a characteristic of an accumulator, and L/R < 1 is an excluder. Accumulators concentrate the metals more in the leaf rather than in the roots. The L/R ratio of the is shown in Table 2.

Table 2. Average leaf/root ratio

Species	Leaf/ Root				
	Cr	Mn	Ni	Cu	Zn
Accacia mangium	0.25	0.5	0.24	0.42	1.09
Casuarina cunninghamiana	0.74	1.83 *	0.95	ND	3.96 *
Ipomoea pes-caprae	0.4	0.61	0.25	0.34	0.27
Lantara camara	0.31	0.47	0.31	0.44	0.38
Leucaena leucocephala	3.72 *	3.61 *	6.15 *	2.55 *	1.93 *
Mimosa pudica	4.24	3.84	6.00	2.38	2.72
Pennisetum polystachion	1.78 *	1.57 *	1.23	ND	1.58 *
Saccharum spontaneum	0.62	0.56	0.53	0.12	1.12
Sphagneticola trilobata	0.74	0.89	0.79	0.97	0.78
Stachytarpheta jamaicensis	0.74	0.54	0.41	0.67	0.91
Turnera angustifolia	0.29	0.72	0.36	0.56	0.83
Crops					
Abelmoschus esculentus	0.21	0.7	0.50	0.17	1.25
Ananas comosus	0.54	1.15	0.19	ND	0.23
Artocarpus heterophyllus	0.03	0.28	0.05	ND	0.17
Basella alba	0.08	0.53	0.27	ND	0.45
Carica papaya	0.21	0.27	0.14	ND	0.62
Chrysophyllum cainito	0.12	0.55	0.31	0.12	0.36
Cocos nucifera	0.14	0.36	0.06	0.22	0.34
Colocasia esculenta	0.25	1.47	0.43	0.20	0.23
Manihot esculenta	0.96	2.94	0.91	1.31	7.00 *
Moringa Oleifera	0.37	1.19	0.58	0.85	1.26
Musa × acuminata	0.06	0.44	0.04	ND	0.29
Selenicereus undatus	0.1	0.2	0.05	ND	0.84
Solanum lycopersicum	0.36	0.79	0.26	1.32	0.84
Solanum melongena	0.47	0.7	0.57	0.11	0.16
Xanthosoma sagittifolium	0.02	0.14	0.04	0.53	0.59

ND – Not detected * Significant hyperaccumulators

Leucaena leucocephala and *Pennisetum polystachion* are significant accumulators of chromium using L/R ratio. *Mimosa pudica* showed L/R > 1; however, the p value is greater than 0.05, The potential of this plant can be confirmed through increasing the sample size for future studies.

For Mn, *Casuarina cunninghamiana*, *Leucaena leucocephala,* and *Pennisetum polystachion, are* found to have significant L/R ratio. *Mimosa pudica*, *Ananas comosus*, *Colocasia esculenta*, *Manihot esculenta*, and *Moringa Oleifera* have L/R > 1, which shows they can be potential hyperaccumulators.

For Ni, only *Leucaena leucocephala* shows significant L/R. Although *Mimosa pudica* with mean 5.9996 but p-value > 0.05 shows great potential to be a hyperaccumulator.

The plant Leucaena leucocephala also shows significant accumulation for Cu and Zn using L/R. Other plants like Manihot esculenta, Pennisetum polystachion, and Casuarina cunninghamiana also shows significant accumulation of zinc. Leucaena leucocephala, can hyperaccumulate all five elements. Mimosa pudica also shows potential hyperaccumulation of all elements. As observed, Cu could not be detected in number of plant species. Cu bioavailability depends on many factors such as Cu level in soil, soil pH, chemical properties of soil, and plants response to the metal, which is either to inhibit the uptake or absorb the metal by developing some tolerance mechanism (17). In this study, the low Cu concentration in the soil is confirmed for some samples like in Casuarina cunninghamiana, Artocarpus heterophyllus, Pennisetum polystachion, and Selenicereus undatus, in which Cu is not detected in the soil samples.

3.3 Evaluation of metal accumulation using BAC, and TF

An ideal plant to be used for phytoextraction are those with Translocation Factor (TF) and Bioaccumulation concentration (BAC) >1 (8). Bioaccumulation coefficient is the measure of metal in the shoot to the metal in soil while Translocation factor is the ratio of metal in the shoot to the metal concentration in the roots. Here the values are evaluated, and the results are shown in Table 3. Based on the results, none of the plants is able to achieve the BAC and TF of 1 for Cr and Mn, The plant *Ipomoea pes-caprae* has BAC = 1 for Ni, which is the only plant to achieve the value. *Manihot esculenta* and *Ipomoea pes-caprae* have BAC > 1 for Zn but none of these is significant.

For TF, the plants that show significant values are Leucaena leucocephala (Mn, Ni, Cu), Casuarina cunninghamiana (Mn), Casuarina cunninghamiana (Zn) and Carica papaya (Zn).

Table 3**.** Bioaccumulation coefficient and translocation factor of the plants

Metal		Species	Result
Mn	BAC	None	
	TF	Casuarina cunninghamiana	2.60
		Leucaena leucocephala	**2.79**
Ni	BAC	None	
	TF	Leucaena leucocephala	**3.53**
Cu	BAC	None	
	TF	Leucaena leucocephala	**1.65**
Zn	BAC	None	
	TF	Casuarina cunninghamiana	**2.71**
		Carica papaya	**1.35**

Significant (Mean > 1.0, $p \leq 0.05$)

In summary, the significant hyperaccumulators of the heavy metals are listed in Table 4.

3.4 Accumulation of metals in the edible part of crops

Most of the mining firms in the Philippines consider planting of crops as an alternative land use for mined-out areas. The areas are planted with crops, and the workers and the people in the community usually consume the harvests. In table 5 is the average metal accumulation in the edible parts of the plant and the permissible values of some metals in water or food. Moreover, some of health implications include: Hexavalent Chromium or Cr (VI) is carcinogenic (IARC) and associated with lung cancer (WHO), Manganese is associated with neurotoxicity, inflammation, and mitochondrial disinfection at high level of exposure (NIH), Copper is linked to gastrointestinal problems, and nickel can elicit dermatitis in some individuals (WHO). For Zinc, there is no reported severe problem that could affect humans.

Table 4. Summary of hyperaccumulator plants

Criteria	Cr	Mn	Ni	Cu	Zn
HMA	Mimosa pudica	None	Chrysophyllum cainito Leucaena leucocephala Mimosa pudica Pennisetum polystachion	None	None
L/R ratio (>1)	Pennisetum polystachion Leucaena leucocephala	Casuarina cunninghamiana. Leucaena leucocephala, Pennisetum polystachion	Leucaena leucocephala	Leucaena leucocephala	Manihot esculenta, Leucaena leucocephala, Pennisetum polystachion, Casuarina cunninghamiana
BAC (>1)	None	None	None	None	None
TF (>1)	None	Leucaena leucocephala Casuarina cunninghamiana	Leucaena leucocephala	Leucaena leucocephala	Casuarina cunninghamiana, Carica papaya

Table 5. Heavy metals in crops

Species	Philippines common name	Part (Permissible values based from FAO/WHO/ NIH)	Cr (35 µg/day for Cr (iii)	Mn (11 mg/day)	Ni (67.9 mg/kg)	Cu (73.3 mg/kg)	Zn (99.4 mg/ kg)
Basella alba	Alugbati	Stem	193	231	230	13	128
		Leaves	187	719	396	0	129
Manihot esculenta	Cassava	Root	110	81	101	0	113
Solanum melongena	Eggplant	Fruit	134	285	169	45	85
Colocasia esculenta	Gabi	Stem	2026	852	1010	19	78
		Leaves	555	1028	748	20	45
		Fruit	91	118	114	45	152
Moringa Oleifera	Malunggay	Stem	210	222	243	19	42
		Leaves	171	532	304	39	88
Xanthosoma sagittifolium	Karlang	Fruit	35	55	77	46	97
Abelmoschus esculentus	Okra	Fruit	60	157	60	16	88
Carica papaya	Papaya	Fruit	154	451	245	43	256
Ananas comosus	Pineapple	Fruit	153	472	247	43	254
Solanum lycopersicum	Tomato	Fruit	90	162	87	46	109

The result shows the highest observed value is 2026 mg/kg for Cr in the stem of *Colocasia esculenta* (gabi), a staple food in the Philippines. This result is for total chromium, but the presence of Cr(VI) cannot be discounted. For Mn, the highest observed value is 1028 mg/kg for *Colocasia esculenta* (gabi) and lowest is *Xanthosoma sagittifolium* with 55 mg/kg. The same plant *Colocasia esculenta* (gabi) is highest in nickel accumulation. *Carica papaya* is the highest accumulator of Zn at 256 mg/kg and followed closely by *Ananas comosus* at 254 mg/kg.

The consumption of the above crops may be acceptable in minimal amounts. But this could be hard to control, especially since these are essential foods. Consumers will never mind the origin of the food if it is already available. Long-term consumption of these crops may also result in health risks. For this reason, agricultural application for mined-out areas is not recommended while the metal level is still too high. Phytoremediation or phytomining is the more favorable option until the level of heavy metals in the soil is reduced to an acceptable value for agriculture.

3.5 Phytoremediation and Phytomining potential

Crops will not be considered and recommended for phytomining or phytoremediation. As discussed in the previous section, crops accumulate heavy metals in their edible parts, and some are hyperaccumulators. It has some implications for human health; hence, their production for phytoremediation or phytomining is not favorable. There is always some risk if the crops are used for phytoremediation because these are foods.

Based on the evaluation, four (4) plants are significant hyperaccumulators of the metals. The list is in Table 6.

Leucaena leucocephala. This plant is endemic to the study area. The estimated biomass can reach up to 200 m^3/ha/year in good soil condition after 3-4 years of planting(18) or 34 Mg/ha/year (19).

Pennisetum polystachion, is a perennial grass which grows well in the study area and even anywhere in the Philippines. Based on the study of Poolakkalody (2021) it has biofuel potential producing an average of 62mg/g of ethanol in leaf.

Table 6. Biomass potential of the hyperaccumulator plants

Species	Findings (significant hyperaccumulation)	Biomass/ Bioenergy potential	Ref.
Leucaena leucocephala	HMA: Ni L/R: Cr, Mn, Ni, Cu, Zn BAC: None TF: Mn, Ni, Cu	10-50 m^3/ha/year 40-200 m^3/ha/year (after 3-4 years)	(18)
		34 Mg /ha/year	(19)
Pennisetum polystachion	HMA: Ni L/R: Cr, Mn, Zn	62 mg/g of ethanol in leaf	(20)
Casuarina cunninghamiana.	L/R: Mn, Zn TF: Mn, Zn	400 kg/tree	(21)
Mimosa pudica	HMA: Cr, Ni	0.0908L/ kg ethanol	(22)

Casuarina cunninghamiana. This plant is commonly used for rehabilitation of mines in the Philippines because they are known to withstand environmental conditions. The estimated biomass of this tree is at 400 kg/tree and harvestable leaves volume of 0.3 m^3/tree (21).

Mimosa pudica is a perrenial flowering plant. A study on its biofuel potential was conducted and 0.09 L/kg ethanol is estimated [19].

Although their phytomining potential will depend greatly on their potential for profit and highly dependent on metal prices and processing cost, the use of these plants for mine rehabilitation, and contaminated soil remediation is recommended. The plants identified as significant hyperaccumulators are in Table 4. These plants may be further studied for their actual biomass and biofuel potential in the mine or areas where phytoremediation or phytomining is considered. Their actual yield and accumulation may differ from literature due to differences in environmental conditions.

3.6 Ways Forward

This study is part of the efforts to utilize the mine waste in the region. The nickel laterite mine waste may be further studied to extract the metals using nanotechnology and use in application such as in increasing efficiency of dye-sensitive solar cells [23], and wastewater treatment [24].

4. CONCLUSION

There are plant species thriving in the mine site which can hyperaccumulate metals. *Leucaena leucocephala, Pennisetum polystachion, Casuarina cunninghamiana,* and *Mimosa pudica* shows promising results in accumulating Cr, Mn, Ni, Cu, and Zn considering the leaf-to-root ratio. The biomass potential of these hyperaccumulator plant species can be further studied in the actual mine site to confirm the phytomining potential of these hyperaccumulator plants.

The crops can accumulate metal in their edible parts, which can be harmful to human if consumed regularly. It is essential to remove or at least lessen the amount of metal in the soil before considering agriculture as an alternative land use for mined-out areas. Phytomining or phytoremediation is recommended as an alternative method to extract metals from low grade mine area and as a method for cleansing the land with heavy metals before agricultural applications.

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