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Phytomining: Using Plants to Extract Valuable Metals from Mineralized Wastes and Uneconomic Resources

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23.1 Introduction

Hyperaccumulators are plants that share the ability to grow on metalliferous soils and to accumulate exceptional concentrations of specific metallic and metalloid elements in their shoots (Reeves 2003; van der Ent et al. 2013a). These plants can be utilized as “metal crops” and grown on unconventional resources to recover strategic metals in phytomining (also called “agromining”) operations (Chaney et al. 1998, 2007; Baker et al. 2010; van der Ent et al. 2013a, 2015a). Although there are currently over 700 plant species identified as metal hyperaccumulators, including arsenic, cadmium, cobalt, copper, manganese, zinc, nickel, thallium, and selenium, over 70% are nickel hyperaccumulators. Furthermore, subeconomic nickel contaminated and mineralized soils cover extensive land areas; hence most research has focused

on the development of nickel phytomining. Large-scale demonstration of nickel phytomining with *Alyssum murale* (yellowtuft) has been undertaken in United States and Albania (Li et al. 2003; Bani et al. 2015a), and substantial potential exists in tropical regions using native “metal crops” (van der Ent et al. 2013b; Nkrumah et al. 2016). Here we discuss the status of phytomining operations with a particular focus on nickel, and highlight the progress our research team has made in providing “real-life” evidence of tropical phytomining.

23.2 Phytomining Technology

Phytomining relies on hyperaccumulators to extract metals in biomass for economic gain rather than pollution remediation (Chaney 1983; Brooks et al. 1998). In this approach hyperaccumulator plants are grown over (spatially large) subeconomic ore bodies or ultramafic soils followed by harvesting and incineration of the biomass to produce a commercial high-grade bio-ore. In the case of nickel, the bio-ore may be turned into a range of different nickel products that may include nickel metal, nickel-based catalysts, and pure nickel salts (Chaney et al. 2007; Barbaroux et al. 2012; van der Ent et al. 2015a).

The nickel hyperaccumulator, *Streptanthus polygaloides* (Brassicaceae), recovered 100 kg ha⁻¹ nickel from ultramafic substrates in initial experiments (Nicks and Chambers 1995, 1998). Similar success was achieved with other hyperaccumulators: for nickel with *Alyssum bertolonii* (Brassicaceae) in Italy (72 kg ha⁻¹ nickel) by Robinson et al. (1997) and *Berkheya coddii* in South Africa (100 kg ha⁻¹ nickel); with a thallium hyperaccumulator, *Biscutella laevigata* (Brassicaceae) in France (8 kg ha⁻¹ thallium); and with gold by induced hyperaccumulation using ammonium thiocyanate in *Brassica juncea* (Brassicaceae) (up to 57 mg kg⁻¹ gold per plant) (Anderson et al. 1998, 1999, 2005). Large-scale field trials with *A. murale* (Figure 23.1) suggest that >100 kg ha⁻¹ nickel could be achieved (Li et al. 2003; Bani et al. 2015a).

Societal pressure to reduce the environmental impacts of conventional mining, technical difficulties in economic recovery of metals from low-grade ores, and high metal prices have contributed to an increased interest in phytomining research (Harris et al. 2009). Compared to strip-mining operations, phytomining has an environmental impact like agriculture or agroforestry and it does not require mine site rehabilitation at the end of life (Harris et al. 2009). Phytomining might also generate renewable energy from the incineration of plant biomass before smelting or hydrometallurgical refining (Anderson et al. 1999). For a detailed life cycle assessment of phytomining supply chain, see Rodrigues et al. (2016).



FIGURE 23.1

Large-scale demonstration of phytomining of nickel with *Alyssum murale* growing on ultramafic substrate in the Balkans (Albania).

23.3 Suitable Sites for Phytomining

The cultivation of “metal crops” could be undertaken on large metal-rich surface areas. For nickel, cultivation is feasible on ultramafic areas with suitable topography, where soils are of poor normal agricultural utility, or degraded nickel-rich land which includes nickel laterite mine sites, smelter-contaminated areas, and ore beneficiation tailings (van der Ent et al. 2015a). Criteria to consider for use of land for phytomining include the ownership arrangements, location outside any protected areas/nature reserves, road accessibility, slope aspect, availability of (gravity) irrigation, and local soil properties.

23.4 Selection of “Metal Crops” for Nickel Phytomining Operations

Only hyperaccumulator plant species that accumulate reasonably high concentrations of nickel (>1 wt. %, but preferably >2 wt. %) in their biomass are suitable as a “metal crop.” Other desirable traits include a high growth-rate and high biomass of the shoot, the ability to thrive in exposed conditions, low irrigation requirements, ease of mass propagation, resistance to disease, and so forth. [Table 23.1](#) lists the nickel species that have been identified as having especially high potential as “metal crops.”

TABLE 23.1
Nickel Metal Crop Species with High Potential for Application as Metal Crops in Nickel Phytomining Operations

Plant Species	Potential Application Area	Native Distribution	Height (m)	Cropping System	Shoot Nickel (wt. %)	References
<i>Alyssum</i> spp.	Mediterranean and Eurasian Region	S & SE Europe, Turkey, Armenia, Iraq, Syria	0.5–1	Perennial herb	1–2.5	(Brooks 1998)
<i>Buxus</i> spp.	Tropical Central America	Cuba	0.3–12	Ligneous shrub	1–2.5	(Reeves et al. 1996)
<i>Phyllanthus</i> spp.	Tropical Asia-Pacific Region	Southeast Asia and Central America	1–6	Ligneous shrub	2–6	(Baker et al. 1992; van der Ent et al. 2015b)
<i>Rinorea bengalensis</i>	Tropical Asia-Pacific Region	Southeast Asia	5–20	Ligneous shrub	1–2.7	(Brooks and Wither 1977)
<i>Berhetea coddii</i>	Southern Africa	South Africa, Zimbabwe	1–2	Perennial herb	1.1	(Morrey et al. 1989)
<i>Pearsonia metallifera</i>	Southern Africa	Zimbabwe	0.35–1.5	Perennial herb	1.4	(Wild 1974)

Source: From Nkrumah, P. N. et al., *Plant Soil*, 406, 55–69, 2016.

Although local plant species are recommended because of their adaptation to local climatic and edaphic conditions (Baker 1999; Bani 2007), there are two species, *A. murale* (Brassicaceae), originating from the Balkans, and *Berkheya coddii* (Asteraceae), originating from South Africa that may be regarded as universal “metal crops” which could be widely used in Mediterranean and Steppe climates, respectively. However, careful climatic matching remains important, as an experiment with *Alyssum* spp. in Indonesia did not yield any useful outcome (van der Ent et al. 2013b). Therefore, the potential exists for *Alyssum* spp. to find application in phytomining operations in nickel-enriched soils of Australia (Queensland), China, Balkans, Iran, Greece, Russia, Turkey, and the United States, while *B. coddii* might be utilised in Brazil, South Africa, the United States, and Zimbabwe. We stress that the possible introduction of these species in these locations must comply with applicable national biosecurity legislation and appropriate crop management. For example, poor management subsequent to the scientific trials with *A. murale* in the United States resulted in the species becoming invasive and eventually being listed as a noxious weed in Oregon (USDA 2015).

23.5 Insights from Laboratory and Field Tests to Maximise Nickel Yields

High biomass production and shoot nickel content of “metal crops” are very important considerations in nickel phytomining. Appropriate agronomic systems have been proposed to maximize the yields of the selected “metal crop” (Li et al. 2003; Bani 2007; Bani et al. 2015a; Nkrumah et al. 2016). Inorganic fertilization plays a significant role in maximizing the growth and metal yield of “metal crops” (Li et al. 2003; Bani 2007; Bani et al. 2015a; Álvarez-López et al. 2016). Phosphorus appeared to have a strong effect on the biomass yield and nickel uptake by hyperaccumulator species growing on soil not previously fertilized, while previously fertilized soils show a lesser response to phosphorus fertilization (Robinson et al. 1997). In Albania, Bani et al. (2015a) found *A. murale* biomass yield was increased 10-fold with 120 kg NPK fertilizer and 77 kg calcium ha⁻¹ plus monocot herbicide to control grasses. Furthermore, these agronomic practices increased nickel phytoextraction yield from 1.7 to 105 kg ha⁻¹.

Broadhurst and Chaney (2016) investigated the effect of organic matter amendments on growth and metal yield of *A. murale*. The authors observed negligible effect on the biomass and yield of the “metal crop.” However, the extreme conditions of some substrates (e.g., industrial waste material or mine spoil) may require the use of organic amendments to improve soil fertility (Séré et al. 2008; Chaney and Mahoney 2014).

Furthermore, the effect of soil pH on nickel accumulation in *Alyssum* spp. is unusual. Whereas increasing soil pH reduces the solubility of nickel, and hence reduces nickel concentration in “normal” crop plant species (Kukier and Chaney 2001), the nickel concentration in the biomass of *Alyssum* increased as soil pH was raised depending on soil properties (Nkrumah et al. 2016).

Beyond fertilizer treatment and pH adjustment, many plant management practices need to be employed to enhance metal yields in phytomining. First, plant density is important to optimize biomass production per unit area, and evidence suggests intermediate density results in optimum nickel yield (Angle et al. 2001; Bani et al. 2015b). Second, weed control minimizes the competition between the “metal crop” and weeds for essential nutrients and water (Chaney et al. 2007; Bani et al. 2015a). Third, Plant Growth Promoting Rhizobacteria (PGPR) might be an interesting option as some PGPR isolated from the native rhizosphere of hyperaccumulators were shown to significantly improve the phytoextraction yield of hyperaccumulator plants grown in inoculated soils in pot experiments (Durand et al. 2016). The management of propagation and harvest will necessarily be dependent upon the species being used for phytomining (Nkrumah et al. 2016).

23.6 Processing of Nickel Biomass and Bio-Ore

Early nickel phytomining trials employed an arc furnace to smelt nickel metal from the bio-ore (Chaney et al. 2007). Recent studies suggest other methods could further capitalize on the “biopurity” of the bio-ore to increase the profitability of nickel phytomining. For instance, the hydrometallurgical processing method could be a suitable alternative to derive higher value products from the bio-ore: (1) nickel catalysts for the organic chemistry industry (Losfeld et al. 2012) and (2) nickel chemicals for the electroplating industry (Barbaroux et al. 2012). Research is still needed to explore more efficient methods to synthesize nickel products from the biomass.

23.7 Tropical Phytomining

Tropical regions (e.g., in the Asia-Pacific region, Indonesia, Malaysia, Philippines, Papua New Guinea, and New Caledonia) have the greatest potential for phytomining as large expanses of ultramafic soils exist (van der Ent et al. 2013b, 2016). Phytomining operations in this region may be a complementary process to existing mining operations, as part of the

progressive rehabilitation process after conventional resource extraction. Agromining could also replace existing marginal agriculture on poor ultramafic soils. The application of agromining is envisaged to provide opportunities for an income source for communities in Malaysia, Indonesia, and the Philippines as an alternative type of agriculture or agroforestry pursuit (“farming for nickel”).

Substantial progress is currently being made in developing nickel phytomining in the Asia-Pacific Region by our research team. We have recently discovered over 20 new hyperaccumulator plant species in Sabah (Malaysia) and Halmahera (Indonesia), which is indicative of the very high potential of this untapped resource in the Asia-Pacific Region (van der Ent et al. unpublished data). From the different hyperaccumulator plant species that have been discovered, suitable “metal crops” are now being selected for agronomic trials to assess growth performance, fertilizer requirements, and sustained nickel yields of the crops when successively harvested. Suitable “metal crops” are selected based on their relative growth rates, nickel accumulation, and effective propagation methods. Currently, experimental studies (Figure 23.2) are undertaken to establish optimal agronomic systems to stimulate biomass production and nickel yield in two prospective species: *Phyllanthus securinegoides* (Phyllanthaceae) and *Rinorea bengalensis* (Violaceae).



FIGURE 23.2

Pot trial undertaken over a period of 12 months in Sabah, Malaysia, with *Phyllanthus securinegoides* (small leaf blades) and *Rinorea bengalensis* (large leaves) to determine optimal agronomic systems for tropical nickel phytomining.

23.8 Potential Lifespan and Economics of Nickel Phytomining

As with all methods for resource extraction, phytomining will be finite due to the diminishing concentrations of nickel in the zone accessible by plant roots (Chaney et al. 2014a, b). Nevertheless, considering soil materials with 0.2 wt. % nickel and “metal crops” with a yield of 100 kg nickel ha⁻¹ the phytomining venture may be sustainable for decades (van der Ent et al. 2015a). Table 23.2 presents the economic potential of nickel phytomining.

We summarize the economic analysis under two main production systems: (1) an intensive system such as demonstrated in the United States (Li et al. 2003), and (2) an extensive system as demonstrated in Albania (Bani et al. 2015a). Here we define an intensive system as a fully mechanized production system where the cost of operation includes costs for seed stock, fertilizers, labor, and equipment, whereas an extensive system mainly employs manual labor in its operation, and the production cost involves the use of fertilizers, herbicides, and complementary agricultural management practices. The production costs in the extensive system are relatively low, and this system is recommended for places with readily available and relatively low-cost manual labor. It is evident that nickel phytomining is a highly profitable agricultural technology for the respective systems. The profitability could increase when recovery of energy of combustion and sale of carbon credits are considered. We stress that nickel metal product is profitable; however, other higher value nickel products such as pure nickel salts may further increase the profitability of nickel agromining in the near future.

TABLE 23.2

Economic Analysis of an Annual Nickel Phytomining Crop

Expense and Income Category	Intensive System (ha ⁻¹ yr ⁻¹)	Extensive System (ha ⁻¹ yr ⁻¹)
Cost of production in 2016	\$1074	\$600
Cost of metal recovery	\$720	\$396
Gross value	\$3600	\$1980
Net value	\$1806	\$984

Economic analysis of an annual nickel phytomining crop per ha under two main production systems: (1) an intensive system such as demonstrated in the USA (Li et al. 2003a) and (2) an extensive system as demonstrated in Albania (Bani et al. 2015a). The cost of production in the intensive system is high, including costs for seed stock, fertilisers, labour and equipment, whereas the production costs in the extensive system are relatively low because it mainly involves the use of fertilisers, herbicides and complementary agricultural management practices. The annual crop nickel yield for an intensive system and an extensive system are 200 and 110 kg ha⁻¹, respectively. The commercial value of nickel of \$18 per kg was estimated as an average value of nickel over a period of 5 years (2010–2015) at the London Metal Exchange. The cost of metal recovery was estimated at 20% of nickel value.

23.9 Conclusions

Phytomining technology has been successfully demonstrated in Mediterranean and temperate climates for nickel using *Alyssum* spp., and our ongoing research in Southeast Asia using *P. securinegoides* and *R. bengalensis* will be critical to provide “real-life” evidence of tropical phytomining. The nickel mining industry needs to test phytomining as a supplement to traditional mining as it uses only a small portion of sub-economic ultramafic soil deposits and could be highly profitable. Nickel phytomining will also improve soil fertility and reduce toxicity due to soil nickel; this is a significant service rendered through phytomining which we then defined as agromining. As such it will make the land suitable for other future usage, including forestry and some types of traditional agriculture. It is envisaged that agromining could also support local livelihoods with income opportunities as an alternative type of agriculture: to farm nickel. The demonstration of phytomining other strategic elements (e.g., cobalt, manganese, rare earths) is underway and should use the same general approach as nickel phytomining.

Acknowledgments

P. N. Nkrumah is the recipient of an Australian Government Research Training Program Scholarship at The University of Queensland. A. van der Ent is the recipient of an Australian Research Council Post Doctoral Fellowship (DE160100429).

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