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PHYTOMINING AND ITS ROLE IN IMPROVING SOIL QUALITY AND RECOVERING SOME CRITICAL RAW MATERIALS

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Abstract. *This paper delves into the process of phytomining, with a particular emphasis on the recovery of heavy metals, notably nickel. It explores the role of various participants in the phytomining process and the factors that influence it. The paper underscores the economic significance of phytomining as a technology for the recovery of critical metals, presenting several case studies on the recovery of these metals, including noble metals, rare earth elements, nickel, zinc, and cadmium. It also provides an in-depth analysis of the environmental and economic impacts of the phytomining process, specifically for nickel, through a life cycle analysis. The paper concludes by identifying the advantages and limitations of phytomining.*

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1. Introduction: Phytomining and its role in improving soil quality and recovering some critical raw materials

The recovery of metals from high biomass plant crops grown in soil substrates, especially those associated with heavy metal pollution by phytomining is a recent, more advanced phytoremediation technology to produce low-volume,

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sulphide-free "bio-ore" that can be safely and further processed if the target metal has significant economic value. This technology also has potential applications in the mining industry for the recovery of heavy metals from poor ores [1]. Commercial metal mining is usually carried out from ores that have a high concentration of target metals, but requires huge capital investment and complex extraction processes. Sub-economic ores are more numerous and the metal content is well below the metal content required to be economically mined and processed by conventional techniques.

Numerous lands around the globe are polluted with metals that could be phytomined. Major scientific advances have been made in recent years in understanding the potential application of this plant-based technique in the mining industry [2]. The link between the extraction of metals from poor ores and plants has been recognized since medieval times, but it was only in the 20th century that it became possible to analyze plant tissues to ascertain high metal concentrations in their biomass [3]. It was thus found that a focal point of the interactions of plants in the soil with the metals that pollute it is the micro-ecosystem that surrounds the roots of the plants - the rhizosphere, determined by different physical, chemical and biological conditions created by the roots of the plants and the surrounding environment of the soil. It is well documented that soil solution is drawn from roots to the aboveground portions of their biomass by plant water uptake, which depends on the root uptake factor, a dimensionless parameter describing the metal concentration coefficient in the xylem/soil solution. Increased understanding of the role of plants in the extraction of metals in the circulation of minerals in the biosphere has been achieved with important biotechnological tools in the process of mining low-grade ores [4].

Plants provide several patterns of response to the presence of high metal concentrations in soil. Most are sensitive to high concentration of metals, especially if they are toxic, and others have developed resistance, tolerance and can bioaccumulate heavy metals in roots and aboveground parts such as shoot, flowers, stems and leaves. Plants with the capability to absorb metal compounds via their root systems may be strategically planted in soils contaminated with metals. After growth, these plants can be harvested, and the extracted metals can be utilized in diverse industrial applications [5, 6]. While the concept of cultivating particular plants to remediate metal-contaminated soil is not novel, what sets recent developments apart is the establishment of commercially feasible methods for extracting metals from these plants. These plants apt for phytomining are referred to as hyperaccumulators due to their propensity to amass significant quantities of metals within their tissues. Most plants do not grow well in metal-contaminated soil, and those that can grow, the hyperaccumulators develop specific tolerance mechanisms [4-6]. Hyperaccumulators efficiently extract metals from metalliferous soils and then translocate them to above-ground plant tissues. After sufficient growth, the plant is harvested and left to dry. The dried plant material is reduced to an ash with or without energy recovery, which is further treated with specific processes, which allow metals from an ash or ore to be recovered according to conventional metal refining methods, such as acid dissolution and electrowinning (Fig. 1). Thus, phytomining performs the *in situ* removal of metals from sub-economic ores or from sites contaminated with metals, with the aim of recovering them from plant biomass under economic conditions [7].

Phytomining is a chain of processes that extract metals from low-grade ores, contaminated soils or wastes and produce compounds with high added value and can decide to face two trends [8, 9]:

(i) Due to the increasing need for metals and the depletion of higher grade ores, which historically were the first to be used due to their profitability, ore grades have undergone a structural decline. As a result, for a given amount of metal extracted, the mining industry faces increased waste generation and land degradation, as well as increased challenges in extracting metals at economically viable costs.

(2) Anthropogenic activities (e.g. mining, industry, urban, waste disposal) can cause the accumulation of heavy metals over large areas, which cannot be treated with conventional depollution practices (e.g. soil excavation). Unless polluted areas are under strong urban development pressure that would allow a rapid return on investment, these techniques are prohibitively expensive and therefore currently unrealistic.

The main objective of the paper consists in the analysis of the phytomining process of some heavy metals, particularly nickel, through the prism of the advantages and impacts it can generate from an economic and ecological point of view.

2. The need to recover some metals from sub-economic sources

2.1. The perspective of the European Commission on critical raw materials

In today's global landscape, there is a growing concern regarding the scarcity of raw materials, with some reaching critical shortage levels, known as **critical raw materials.** As highlighted in documents from the European Commission, raw materials play a key role in the economy of Europe [10], serving as the foundation for a robust industrial sector that produces a wide array of goods essential for everyday life and modern technologies. The unrestricted availability of certain raw materials has become a pressing issue not only within the European Union but also on a global scale. In response to this challenge, the European Commission has compiled a list of critical raw materials (CRMs) for the EU, subject to periodic review and updates. CRMs encompass raw materials deemed crucial for the EU economy, yet pose high risks in terms of their supply. These critical raw materials hold particular significance for several reasons, as outlined by the European Commission:

- *Industry linkage:* Non-energy raw materials are intricately linked to various industries across the entire supply chain spectrum.
- *Technological advancement:* The progression of technology and improvements in quality of life hinge on access to an expanding array of raw materials.
- *Environmental impact:* Raw materials play a crucial role in facilitating clean technologies, being essential components in solar panels, wind turbines, electric vehicles, and energy-efficient lighting solutions.

This is why to respond to the growing concern about securing valuable raw materials for the EU economy, the European Commission launched *The European Raw Materials Initiative* in 2008. This is an integrated strategy that sets out specific measures to ensure and improve access to raw materials for the EU. One of the priority actions of the initiative was the establishment of the EU-wide list of critical raw materials (CRM). The fact that the latest list of essential raw materials for the EU was adopted together with the renewed EU Industrial Policy Strategy on 13 September 2017 reflects the high importance that the Commission continues to attach to the list. The Commission is also engaged in a Critical Raw Materials Dialogue with the US and Japan – the seventh annual meeting and conference was held in Pittsburgh on 12 October 2017 [10].

CRMs are especially important for high-tech products and emerging innovations - technological progress and quality of life depending on access to an increasing number of raw materials. For example, a smartphone can contain up to 50 different metals, all of which offer different properties, such as light weight and easy-to-use small size. CRMs are irreplaceable in solar panels, wind turbines, electric vehicles and energy-efficient lighting, and are therefore also highly relevant to combating climate change and improving the environment. For example, the production of low-carbon technologies – needed for the EU to meet its climate and energy targets is expected to increase demand for certain raw materials by a factor of 20 by 2030 [11]. The Critical Raw Materials List contains raw materials that meet or exceed thresholds for both economic importance and supply risk. The Commission established the first list in 2011 and undertook to update it at least every three years to reflect market, production and technological developments [10]. The first evaluation, carried out in 2011, identified 14 CRMs from the 41 non-energy, non-agricultural raw materials evaluated. In 2014, 20 raw materials were identified as critical out of the 54 materials evaluated. In 2017, 27

CRMs were identified using a revised methodology for the evaluation of 61 raw materials (comprising 58 individual materials and 3 grouped materials, totaling 78 individual materials).

The revised methodology brought several improvements: systematic verification of the most critical points in the supply chain (mining/extraction and processing/refining); the inclusion of an import dependence parameter and a trade-related parameter based on EU export restrictions and trade agreements; also taking into account the actual supply of the material to the EU (domestic production plus imports), not just the global supply; including substitution in both supply risk and economic importance and improving calculations, whereas previous assessments only referred to substitution in supply risk; specific allocation of raw materials to relevant end-uses and corresponding production sectors instead of mega-sectors, etc. [12].

2.2. The global situation in the supply and trade of critical raw materials

European industry is dominated by the manufacturing industry involving the manufacture of finished products and applications and also the refining industry (metallurgy etc.), and less by the extractive industry (mines and transporters). The value chain of CRMs is not fully and homogeneously covered by the European industry. Therefore, there is a pronounced imbalance between the upstream stages (extraction/processing) and the downstream stages (manufacturing and use). Given the very limited supply of CRM from secondary sources, the need for access to primary sources including ores, concentrates, processed or refined materials is huge and crucial for the development and even survival of European industries, associated jobs and economic benefits.

Unfortunately, most of these primary raw materials are produced and supplied from non-European countries. Although China is also the main supplier of CRMs to the EU, the analysis highlights several other countries that represent important shares of the EU supply of certain CRMs, such as the US (beryllium and helium), Russia (cobalt and scandium) and Mexico (fluorspar and tungsten) (Fig. 1). For many CRMs, the upstream stages of the value chain are not present in the EU: antimony, beryllium, borates, magnesium, niobium, PGMs, phosphorus, rare earths, scandium, tantalum and vanadium. This is due either to the absence of those materials in European soil, or to economic and societal factors that negatively affect exploration (for the discovery and characterization of deposits, estimation of resources and reserves) or extraction (closure of existing mines, reluctance to open new mines etc.). To access these primary CRMs, the EU currently has no choice but to import ores and concentrates or refined materials from other countries to supply its industries and markets. Although several CRMs have a high real technical and economic potential for recycling, and despite governments' encouragement to move towards a circular economy, the recycling input rate (a measure of the share of secondary sources in the supply of raw materials) of CRMs is generally low [13]. This can be explained by several factors: sorting and recycling technologies for many CRMs are not yet available at competitive costs; the supply of many CRMs is currently locked in long-lived assets, therefore involving delays between production and scrapping, which negatively influence current recycling rates; the demand for many CRMs is increasing in various sectors and the contribution of recycling is largely insufficient to meet the demand.

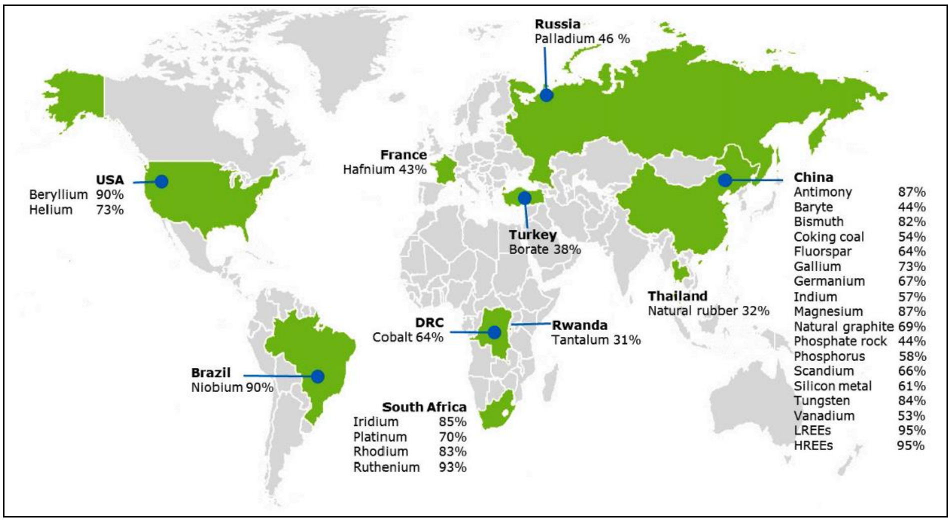

Fig. 1. Contribution of countries with the largest share of primary CRM supply to the EU, average 2010-2014 [10]

3. Participants in the heavy metal phytomining process

Hyperaccumulating plants were discovered in the 1970s [14]. These plants have the ability to extract metals from the soil and accumulate large amounts in their tissues through a process called phytoextraction. First of all, these plants can be considered as indicators of the presence of metals in the soil, but immediately the idea of their application in soil remediation arose. In a second step, it was found that metals present in plant biomass can be recovered, and this technique was called phytomining [7]. Phytomining of heavy metals from soil basically has two essential objectives [15, 16]:
- metal extraction
- soil depollution

In this context, phytomining of heavy metals involves the following participants
- soils polluted with heavy metals
- plants as hyperaccumulators of heavy metals

- the process of extracting metals from the soil and accumulating them in plants (phytoremediation)
- technologies for recovery and refining of metals from plant biomass

3.1. Soils polluted with heavy metals

Soils polluted with heavy metals have become common across the globe due to increased geological and anthropogenic activities. Although heavy metals are naturally present in soil, geological and anthropogenic activities increase the concentration of these elements to levels harmful to both plants and animals. Some of these activities include the mining and smelting of metals, the burning of fossil fuels, the use of fertilizers and pesticides in agriculture, the production of batteries and other metal products in industries, sewage sludge and municipal waste disposal [2, 17].

Heavy metals are natural components of the earth's crust and essential elements, some of which are considered *trace elements* for maintaining the metabolism of flora, fauna and the human body (for example, copper, selenium and zinc). However, at concentrations exceeding natural values, heavy metals are known to be toxic and/or carcinogenic. Heavy metals can pollute the environment because they are involved in various activities unsustainable industrial (https://www.amazon.ca/Mineral-Commodity-Summaries-Geological-Survey/dp/B084DQNRP5). For example:

- *nickel* is used in the manufacture of stainless steels and non-ferrous alloys as well as in galvanizing, or as a catalyst;
- *cadmium* and cadmium compounds are used in the processes of metal coatings (cadmium), obtaining alloys, manufacturing nickel and cadmium batteries, pigments;
- *cobalt* is used for the production of magnetic alloys, electroplating, the manufacture of Li-Co batteries;
- *copper* is used in construction, electricity transmission, manufacturing of electronic products, production of industrial installations;
- *lead* is used in the manufacture of alloys, in construction, obtaining paints;
- *zinc* is used to obtain zinc alloys, brass and bronze as well as in the galvanizing process.

The rapid development of the industry implicitly led to the pollution of the environment with heavy metals, from the following sources (Table 1): industrial waste (textile and pharmaceutical industry), electronic waste, pesticides, fertilizers, sewage sludge. At the European level, approximately 137,000 km^2 of agricultural land require local assessment as well as remedial action as a result of heavy metal pollution [18].

Therefore, the remediation of polluted soils it is an absolutely necessary measure for solving current problems in industry, agriculture, health. Heavy metals in soil mean heavy metals in plants too. The main reaction of plants is the production of reactive oxygen species (ROS) when exposed to high levels of heavy metals. Through soil, metals reach plants and water. In water, heavy metals arrive not only from the soil, but also from the environment. Aerosol particles are present in the atmosphere; they end up in water, soil, soil to plants and surface water. All of these are related and all affect each other. The high concentration of heavy metals in the soil means high concentrations in the environment, in general and in the surroundings, which is a global threat. Heavy metals are not easily removed, but can be easily extracted by plants under suitable conditions [19].

Table 1. Sources of soil pollution with heavy metals (https://ec.europa.eu/environment/industry/stationary/e-prtr/evaluation.htm)

Industrial sector	Amount of metals released into the soil (kg)					
	Ni	Cu	Zn	Cd	Pb	Ag
Waste and wastewater management	155	1670	5080	24.3	371	-
Chemical industry	103	-	609	-	-	-
Processing of ores	61	822	729	-	32	29
Energy sector	-	-	-	-	-	14.7
Total	319	2490	6420	24.3	403	43.7

3.2. Plants and heavy metal uptake - phytoremediation

Heavy metals that plants can absorb are typically those found in soluble form within the soil solution or those that can be easily solubilized by root exudates. While certain heavy metals are essential for plant growth and maintenance, excessive levels of these metals can pose toxicity risks to plants. The same mechanisms that allow plants to accumulate necessary metals also make them susceptible to acquiring non-essential ones. Given that metals cannot be metabolized by plants, when concentrations exceed optimal levels, they can negatively impact the plant's health both directly and indirectly [20, 21].

Phytoremediation is a bioremediation technology that uses living plants to reduce the amount, toxicity and mobility of pollutants in soil through different mechanisms [22, 23] (Fig. 2):

- *phytoextraction* (the ability of plants to absorb pollutants from the soil with roots, followed by their translocation and accumulation in stems and leaves) ;
- *phytovolatilization* (absorption of pollutants from the soil, followed by their transport through the xylem, their transformation into a less toxic volatile form and release into the atmosphere);
- *phytostabilization* (the use of plants to reduce the mobility of metals in the contaminated soil by accumulating them in the roots);

- *phytofiltration* (similar in mechanism to phytoextraction, with the mention that it is applied for the removal of metals from surface waters, groundwater, wastewater);
- *phytodegradation* (the process of metabolizing organic pollutants based on enzymatic activity);
- *rhizodegradation* (biodegradation of pollutants in the rhizosphere area with the help of naturally existing microorganisms).

This technology can be successfully applied to treat soils contaminated with low to moderate metal concentrations by cultivating fast-growing plants that produce large amounts of biomass and achieve efficient absorption of heavy metals from the soil. Other strategies aim at the use of microorganisms (fungi that form mycorrhizae - FM and bacteria that promote plant growth - PGPB) that have the role of protecting and stimulating plant growth under the action of stress factors.

The mechanism of plant development on a contaminated site led to their classification, from the point of view of the relationship with heavy metals in the soil, as follows: exclusions, indicators and accumulators/hyperaccumulators. Accumulator/hyperaccumulator plants are able to grow in soils or waters polluted with very high concentrations of metals, absorbing them through the roots and concentrating extremely high levels of metals in their tissues [24]. Hyperaccumulative plants are used, especially in phytoextraction processes. The successful application of these plants is related to their ability to ensure a fast growth rate, high biomass, to extract and accumulate large amounts of heavy metals in their roots and to translocate them to the plant tissues without suffering phytotoxic symptoms [25, 26]. According to data from the specialized literature, until now about 700 taxa have been identified as hyperaccumulators of one or more metals, of which more than 80% are Ni hyperaccumulators (about 25% belonging to the *Brassicaceae family*) [5, 16, 27].

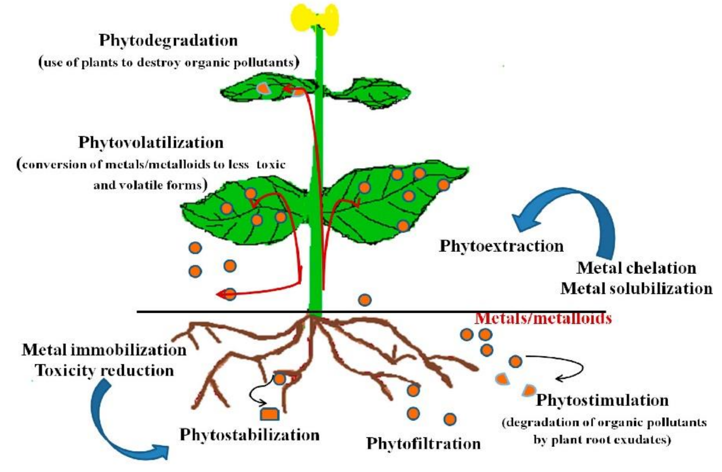

Fig. 2. Mechanisms of phytoremediation

Other hyperaccumulator plants were reported as hyperaccumulators of Co, Cu, Mn or Zn, but fewer for Cd, Ar and Pb (53 for copper, 42 for cobalt, 42 for manganese, 20 for zinc, 7 for cadmium, 5 for arsenic, 7 for lead) [5, 6, 27, 28]. The main representative plant species belong to the following families: *Asteraceae, Brassicaceae, Caryophylaceae, Cyperaceae, Fabaceae, Euphorbiaceae, Lamiaceae, Phyllanthaceae, Poaceae, Pteridaceae, Flacourtiaceae, Verbenaceae* and *Violaceae* [5, 29] (Table 2).

Table 2. Examples of heavy metal hyperaccumulating plants

Metals	Plant species	Family	Metal concentration (mg/kg)	References
Nickel	*Alyssum bertolonii*	*brassicas*	13400	[29]
	Berkheya coddii	*asteraceae*	17000	
	Stackhousia tryonii	*celastraceae*	41300	[30]
	Alyssum murals	*brassicas*	300000	
	Helianthus annuus	*asteraceae*	10700	[31]
Cobalt	*Haumaniastrum robertii*	*lamiaceae*	10200	[29]
	Alyssum troodi	*brassicas*	2325	[9]
	Celosia trigyna L	*amaranthaceae*	501	[32]
	Alyssum corsicum	*brassicas*	1080	
	Vernoniastrum latifolium	*asteraceae*	549	
Copper	*Haumaniastrum katangense*	*lamiaceae*	8356	[29]
	Ipomoea alpina L.	*convolvulaceae*	12300	[25]
	Aeolanthus biformifolius	*lamiaceae*	13700	[33]
	Polypogon fugax	*poaceae*	4012	[32]
	Agrostis stolonifera	*poaceae*	1000	
Zinc	*Thlaspi calaminer*	*brassicas*	10 0000	[29]
	Arabis paniculata	*brassicas*	20800	[9]
	Thlaspi caerulescens	*brassicas*	19410	[34]
	Sedum alfredii	*crassulaceae*	13799	
Cadmium	*Thlaspi caerulescens*	*brassicas*	3000	[29]
	Panicum virgatum	*poaceae*	280	[35]
	Tagetes patula	*asteraceae*	324	[36]
	Helianthus annuus	*asteraceae*	580	[37]
	Arabis paniculata	*brassicas*	1662	[38]
Lead	*Thlaspi rotundifolium*	*brassicas*	8200	[29]
	Brassica juncea L. *Czern*	*brassicas*	103000	[25]
	Noah mucronata	*amaranthaceae*	1485	[39]
	Helianthus annuus	*asteraceae*	1800	[35]
	Goddess Mays	*poaceae*	10600	[40]
	Brassica juncea	*brassicas*	1670	[41]
	Helianthus annuus	*asteraceae*	51000	
thallium	*Iberis intermedia*	*brassicas*	4055	[29]
Gold	*Brassica juncea*	*brassicas*	10	[29]
	Berkheya coddii	*asteraceae*	10	

arsenic	*Agrostis stolonifera* L.	*poaceae*	1350	[31]
	Helianthus annuus	*asteraceae*	1550	
Manganese	*Polygonum perfoliatum* L.	*polygonaceae*	18342	[25]
	Macadamia neurophylla	*proteaceae*	55000	[29]

The major concern of researchers regarding the implementation of phytoextraction is the disposal of plant biomass after the phytoextractive process. As a rule, phytoextraction is followed by harvesting and incineration of plant phytomass. The resulting ash is usually stored under controlled conditions (unsustainable solution) or is used as a fertilizer to improve the soil with trace elements. One of the most widespread approaches in this direction aims to process it through compaction, composting, combustion, gasification and pyrolysis to transform biomass into renewable energy [17, 42, 43].

3.3. Factors influencing phytomining

The success of a phytomining process is highly dependent on the adequate yield of the biomass and the high metal content extracted, as well as the method applied to isolate the metal from the biomass. It follows that both the increase in the bioavailability of metals so that they can be more easily absorbed by plants, but also in the biomass of plants, must be intensified by methods associated with both plants and the soil. To date, a number of studies have focused on laboratory or greenhouse experiments examining the performance of plants in phytomining and phytoremediation processes. However, since field trials can better examine remediation effectiveness because they simulate the true nature of the problem, results from field-scale studies are more useful in practical applications of phytomining.

● *Factors associated with plants* as hyperaccumulators were identified, among others, by Jaffré et al (1976), who observed nickel accumulation in *Sebertia acuminate* [14]. Hyperaccumulating plants are widespread in the plant kingdom. Almost 400 plant species, around 45 plant families are reported as metal hyperaccumulators. A plant is considered as a heavy metal hyperaccumulator, among others, under the following conditions [44, 45]:

a) the minimum metal concentration in the stems of a hyperaccumulating plant for the metals Pb, Cu, Ni and Co must be greater than 1000 mg/kg; for Zn and Mn, greater than 10 000 mg/kg; for Au of 1 mg/kg, and for Cd greater than 100 mg/kg.

b) metal concentrations in the aerial parts of plants must be 10-500 times higher than in the same plant species grown in unpolluted environments [46].

The intensive use of *Brassica species* in phytoremediation (mainly - phytoextraction) results from their intrinsic tolerance to heavy metals and considerable biomass production. Several species of plants from the *Brassicaceae* *family* are known to have the ability to accumulate metals and have been evaluated as potential plants for phytoextraction. For example, according to the results obtained by Dhiman et al. (2017), *Brassica napus* L. (rapeseed) can be considered a potential heavy metal hyperaccumulating plant, showing a high affinity for zinc [47] (Table 2).

● *Factors associated with soil* include:

a) Soil pH: soil acidity-alkalinity is an essential factor that influences both the bioavailability of nutrients necessary for plant growth and the solubility of heavy metals. In the phytoextraction mechanism, it was found that a slight acidification of the soil increases the solubility of metals, favoring their absorption by plants, so the lower pH limit for the development of most plants is 4.5 [7, 48].

b) Soil salinity: it influences the phytoremediation process, affecting plant growth by inhibiting the uptake of water from the soil solution, leading to the occurrence of osmotic stress [7, 48].

c) Soil texture (sandy, loamy, clayey): the bioavailability of heavy metals in the soil depends on the soil texture. Clay content can significantly affect the availability of heavy metals and their subsequent toxicity to living organisms. Crops on a sandy soil are deficient in metals, especially Zn, compared to clay texture; this is due to the large pore size and low holding capacity of the sandy soil for metal retention. In sandy soils, heavy metals can easily move from one horizon to another compared to clayey soils [2, 7, 49].

d) Soil moisture : absorption of heavy metals is greater at high levels of moisture. Plants also produce higher biomass, which further favors the amount of metal extracted from the soil [2, 7, 49].

● *Increasing the bioavailability of metals in the presence of nutrients, chelating agents*

The availability of metals in soil can be improved by the addition of chelating or acidifying agents, as well as agents produced and exuded by plant roots and rhizosphere microorganisms [27]. Fertilization is considered the most effective way to increase biomass production, which is essential for phytomining, so in order to promote plant growth, it is necessary to add nitrogen and phosphorus fertilizers. Nitrogen fertilizers increase phytoextraction of metals such as Zn, Cd, Pb, As. The chemical form of fertilizers will directly influence soil pH which in turn influences metal bioavailability. Ammonium (NH_4^+) can enhance phytoextraction by lowering soil pH [48]. Chelating agents include EDTA (ethylenediaminetetraacetic acid), HEIDA (hydroxyethyliminodiacetic acid), NTA (nitrilotriacetic acid), CA (citric acid), DTPA (diethylenetriaminopentaacetic acid), and thiocyanates [7]. Although chelating agents can enhance the uptake of metals by plants, they should not be applied in excessive amounts, as exceeding the levels of chelators can lead to metal immobilization [48].

4. Applications of phytomining for the recovery of critical metals from soils

4.1. The economic importance of phytomining as a recovery technology for some critical metals

An economically and ecologically important application of phytoremediation/ phytoextraction is phytomining or metal extraction using plants. As mentioned above, phytomining is the process by which hyperaccumulating plants are able to accumulate high concentrations of metals in stems and leaves from contaminated soils, with the aim of subsequently recovering them from biomass [50]. Thus, the phytoextraction and phytoaccumulation of metals with the help of hyperaccumulating plants is the mainstay in the phytomining process, especially when conventional mining is not economically viable, usually due to the low concentrations of metals in ores [27].

Phytomining has been applied to a variety of metals that are of relatively high value. Anderson et al. (2005) used Indian mustard and maize to extract gold (Au) from an oxidized ore pile after treatment with cyanide and thiocynate (induced hyperaccumulation) [51]. The field test showed that Indian mustard (*Brassica juncea*) can concentrate Au from 0.6 mg/kg to 39 mg/kg. Combining field test results with laboratory and greenhouse experimental results, they suggested that phytomining would be economically viable if the soil contained Au at concentrations exceeding 2 mg/kg, assuming that harvested biomass could reach 10 t/ha and the concentration of Au in the biomass would reach 100 mg/kg dry matter. Therefore, the plants used in phytomining must show a good capacity to accumulate a large amount of metals in the tissues, grow quickly, and have a branched root system. The possibility of being harvested easily as well as obtaining a high amount of biomass are other important aspects for the success of phytomining [52]. This technology is usually applied to recover metals with a high commercial value (Ni, Zn, Co, Cu, Au, Ag, Ti) [7, 29, 48], from polluted soils, mining tailings, industrial sludge or mineralized soils [16]. Phytomining represents a feasible technology that involves lower costs compared to conventional methods and that integrates the phytoremediation of contaminated soils with the recovery of critical raw materials as secondary resources – critical metals. The economic importance refers to the fact that these critical metals are used in almost every type of industrial manufacturing process. Some heavy metals such as cobalt, magnesium, chromium, platinum group metals, vanadium etc. are classified as critical raw materials, together with others such as cadmium, nickel, gold, with a high economic importance in Europe, since the production in the European Union represents only 8.6% of the total world production. After harvesting the plants, the plant biomass used in phytoremediation can be used for energy purposes as well, either by burning the phytomass or by generating biogas through anaerobic microbial fermentation. Also, plants that have extracted heavy metals from polluted soils can be used directly as amendments to poor, degraded soils. This method of recovery can help meet the requirements of nutrients containing the nitrogen-phosphorus-potassium (NPK) combination [16, 21, 27, 29].

Phytomining technology was proposed for "metal mining" as early as 1989 by Alan Baker and Robert Brooks [53], with a first demonstration of its economic feasibility in 1995 for nickel using the hyperaccumulating plant *Streptanthus polygaloides* (family *Brassicaceae)*. Then there were a number of investigations into plants growing in soils containing high concentrations of metals (either naturally or due to environmental pollution) or mineral waste. Thus, in addition to Ni hyperaccumulating plants, tobacco plants were used for gold extraction and *Miscanthus* or *Salix species* for palladium extraction [27]. Nickel has a high economic value, so phytomining focused initially – and continued – on the recovery of nickel from hyperaccumulating plants belonging to the *Brassicaceae family* and the genus *Alyssum* (for example: *Alyssum murale* can accumulate up to 20,000 mg/kg metal obtaining an amount of biomass of 10,000 kg/ha harvested during one year) [1, 29, 54] The first patented and commercially available technology was reported by Li et al. (2003) for Ni exploitation by using Ni hyperaccumulating species and *Alyssum ecotypes* [55]. To achieve an efficient technology, the researchers provided a comprehensive program, proposing optimal soil and crop management practices, cultivation of wild plant species, efficient harvesting and biomass processing methods, and Ni recovery methods. As final biomass processing methods, plants are usually incinerated to obtain ash. For example, nickel is ten to twenty times more concentrated in ash than in plant. Further, the ash can be fed into smelters to produce nickel through pyrometallurgy. Ash can also be processed by hydrometallurgy [54].

The phytomining process comprises a series of essential steps [56]:
- identification of soils polluted with metals (metals with high economic value);
- selection of the plant species with high biomass yield and the ability to accumulate large amounts of metal and to tolerate other coexisting metals;
- the application of chelating agents to increase the bioavailability of the metal (where necessary);
- harvesting the plants when they reach maturity;
- application of metal recovery techniques.

The main techniques for recovering metals from hyperaccumulating plants are [27, 30] (Fig. 3):
- *incineration of biomass* - is the most frequently used method, followed by ash melting in order to recover the metal;

- *digestion of biomass* with the help of chemicals followed by further processing depending on the type of metal (for example: electroextraction or extraction with a solvent);
- *anaerobic microbial fermentation* (digestion of biomass with the help of microorganisms) which, in addition to metal recovery, also involves obtaining renewable energy (biogas), as well as the possibility of recovering nutrients that can be used as fertilizer for agricultural soils.

In this context, metals phytomining offers a promising possibility for metal extraction in places where traditional mining activities or recovery of metals from low-grade minerals are not competitive. Therefore, in addition to conventional mining, worldwide attention has been paid to the production of metals from secondary resources that reinforces the circular economy. Accumulation of metals in plants is the first step, through phytoextraction. This is followed by increasing the metal concentration through the enrichment step. Finally, methods are applied to extract metals from biomass (incineration ash) [57].

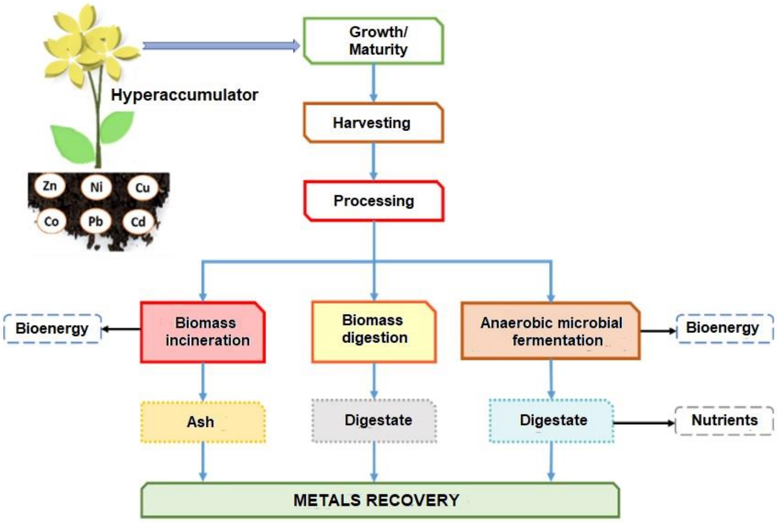

Fig. 3. The stages of the phytomining process

4.2. Gold phytomining

The first gold phytomining experiment was carried out by Anderson et al. (1998) under greenhouse conditions, using *Brassica juncea* (Indian mustard) as a hyperaccumulator, which was treated with ammonium thiocyanate (NH_4SCN) at a rate of 0, 80, 160, 320 and 640 mg kg^{-1} in the substrate of sand containing gold at a concentration of 5 mg kg^{-1} [58]. *Brassica juncea* plants accumulated gold in their aerial parts up to 57 mg kg$^{-1.}$ Msuya et al. (2000) induced hyperaccumulation in five crops (carrot, beetroot, onion, radish) with chelating agents, i.e. ammonium thiocyanate NH_4SCN and ammonium thiosulfate $(NH_4)_2S_2O_3$ in the same artificial substrate consisting of 3.8 mg kg^{-1} gold [59]. The results showed that gold concentrations in the roots of all five crops were higher than in the above-ground parts of the plants. In addition, the average gold concentrations of carrot roots, radish roots were 48.3; 102-113 mg kg^{-1}.

During 2005, the first field trial of phytoextraction of gold from mine tailings was carried out. In this work, *Brassica juncea* (Indian mustard) and *Zea mays (maize)* plants grown on an oxidized ore pile containing 0.6 mg kg^{-1} gold were treated with chemicals (KCN, NaCN) to induce gold hyperaccumulation. The highest gold concentrations of 20 and 39 mg kg^{-1} in *Zea mays* and *Brassica juncea* plants were achieved after KCN application, respectively [51].

A study published in 2011 showed that *Helianthus annus* (sunflower) plants could accumulate average gold concentrations of 14.9; 21.5; 19.2 mg kg^{-1} in roots, stems and leaves, respectively. In this study, the mine tailings substrate had a gold concentration of 2.35 mg kg^{-1}, and NaCN (sodium cyanide) was added at a ratio of 1 mg kg^{-1} to promote gold solubility and to improve gold accumulation in plants [60].

An experiment developed in 2014 tested the ability of three plant species namely *Cyperus kyllingia* (sedge), *Lindernia crustacea* (false pimpernel), *Paspalum conjugatum* (carabao grass) to accumulate gold from cyanidation tailings containing 1.68 mg kg $^{-1}$ Au. Sodium cyanide (NaCN, 1 g kg $^{-1}$) and ammonium thiosulfate ($(NH_4)_2S_2O_3$, 2 g kg^{-1}) were added to induce accumulation in plants. However, gold concentration only reached a maximum value of 0.602 mg kg^{-1} in *Paspalum conjugatum shoot* under ammonium thiosulfate amendment [61].

Another phytoextraction field study was reported by Krisnayanti et al. (2016) [20]. Tobacco grown on a cyanidation substrate consisting of 1.03 mg kg^{-1} Au and 18.2 mg kg $^{-1}$ Ag was treated with 0.05 g kg $^{-1}$ NaCN (sodium cyanide). Under field conditions, average concentrations of gold and silver in tobacco reached levels of 1.2 and 54.3 mg kg^{-1}, respectively.

González-Valdez et al. (2018) evaluated the viability of *Brassica napus* (rapeseed) for extracting gold from mine tailings containing 0.5164 mg kg^{-1} Au [62]. Gold concentration could reach levels of 1.5 mg kg^{-1} in stems and 10 mg kg^{-1} in roots under the effect of NH_4SCN (ammonium thiocyanate). The concentration of gold in the roots is about seven times higher than in the shoots of the plant.

4.3. Silver phytomining

Silver accumulation in plants (*Euphorbia macroclada* (spurge), *Verbascum cheiranthifolium Boiss* (Scrophulariaceae), *Astragalus gummifer* (legumes)) was reported by Sagiroglu et al. (2006) [63]. Terrestrial plants from a polluted mining area contained maximum silver concentrations of 0.97 mg kg^{-1} in the shoot and 3.12 mg kg^{-1} in the root of the growing plant. Borovicka et al. (2007) revealed that the macrofungal species *Amanita* could naturally hyperaccumulate silver from non-argentiferous zones containing 0.07-1.01 mg kg^{-1} Ag [64]. Silver concentrations in *Amanita* species were typically in the range of 200-700 mg kg^{-1}, with the highest value being 1253 mg kg^{-1} Ag. Natural phytomining of silver is viable, but its feasibility under more realistic natural conditions, in combination with microorganisms, as fungi, which has yet to be demonstrated.

Lupinus sp. (blue lupine) reared on base metal mine tailings accumulated 126 mg kg $^{-1}$ of silver in aerial tissues in experiments by Anderson et al. (2003) [65]. *Brassica juncea* accumulated 12.4% silver when exposed to an aqueous substrate containing 1000 mg L^{-1} $AgNO_3$ for 72 h. *Medicago sativa* accumulated up to 13.6% silver when exposed to an aqueous substrate containing 10,000 mg L^{-1} $AgNO_3$ for 24 h. Silver was stored as discrete nanoparticles in both cases with an average size of about 50 nm. It was thus demonstrated that the use of plants to synthesize a large number of metal nanoparticles is viable [52].

4.5. Palladium phytomining

Among the group of platinum metals, palladium is in great demand in various fields. The palladium phytomining concept is however somewhat new, having been monitored for the last decades. The viability of the phytoextraction approach to this valuable element has recently been demonstrated.

Fuchs and Rose (1974) are doubtless the first authors to provide evidence of the accumulation of this valuable metal in plants when 285 µg kg^{-1} Pd was detected in the shoot ash of *Pinus flexilis* (limber pine) [66]. Five years later, Kothny (1979) found concentrations of 400 µg kg^{-1} Pd in ash of *Quercus chrysolepsis* (oak) collected from a sampling site containing 140 µg kg^{-1} Pd [67]. In another work, Nemutandani et al. (2006) evaluated the feasibility of the native plant *Berkheya coddii* (Asteraceae) for phytoextraction from a contaminated area containing 70 µg kg^{-1} Pd [68]. Under natural conditions, palladium was obtained in the roots and leaves of this plant at a concentration of 180 and 710 µg kg^{-1}, respectively.

4.6. Platinum phytomining

Although the ability of plants to accumulate platinum has been mentioned since the 20th century [66], many studies on it have been reported in recent decades. Nemutandani et al. (2006) showed that *Berkheya coddii* (Asteraceae) taken from contaminated sites containing 0.04 mg kg^{-1} Pt could concentrate 0.22 and 0.18 mg kg^{-1} platinum in leaves and roots, respectively [68]. In another study, Walton (2002) found 0.183 mg kg^{-1} of platinum from the same *Berkheya coddii plant* grown on mine tailings [69]. Recently, in 2018, a concentration of 3.06 mg kg^{-1} Pt was reported in terrestrial plants collected from decommissioned contaminated land [70]. There have been several studies that have focused on platinum accumulated by plants in the vicinity of roads. Diehl and Gagnon (2007) found the highest platinum concentration of 14.6 mg kg^{-1} in *Daucus carota* (wild carrot) collected along a busy country highway [71]. Kińska and Kowalska (2019) evaluated platinum accumulation by *Sinapis alba* (white mustard) [72]. The platinum concentration in the root of white mustard could reach up to 5973 mg kg^{-1} when this plant was grown in a nutrient solution containing 1.0 mg L^{-1} Pt for 2 weeks. Despite many reports of platinum in plants, platinum accumulation in phytomining experiments has not been performed.

4.7. Phytomining of rare earth elements

The rare earth elements (REEs) are a group of 17 chemically similar metallic elements in the Periodic Table, including scandium (Sc), yttrium (Y), and 15 "lanthanide" elements, from lanthanum (La) to lutetium (Lu). The terms rare earths and rare earth metals or minerals are also used. The growing demand for rare earth elements for modern industry has led to an increase in mining activities and consequently released these metals into the environment. Increasing the concentration of these elements in a habitat has an impact on its ecosystem, but on the other hand, it also provides the opportunity to be recovered from low-grade minerals. Phytomining is proving to be an ecologically sound technique to extract these valuable elements from contaminated soils where traditional mining is not competitive.

Among plants with unusual accumulation of rare earth elements, the fern was known as a hyperaccumulator with major potential for lanthanides (La and Ce) in a Japanese investigation involving 96 fern species [73]. In general, most studies have focused on *Dicranopteris linearis*, a fern species commonly found in tropical and subtropical climate regions. The first report of probably the exceptional concentration of REE in this plant was published by Wang et al. (1997) [74]. The work showed that fern leaves harvested from plants growing in a rare earth ore mining area could contain 3358 mg kg^{-1} of 8 rare earth metals, including La, Ce, Nd, Sm, Eu, Tb, Yb and Lu. Zhenggui et al. (2001) analyzed *Dicranopteris linearis plants* taken from four different substrates such as a light mining area enriched with EER, a heavy mining area enriched with EER, both heavy and light areas enriched with EER [75]. The highest whole EER levels of 2271, 1570, 459 mg kg^{-1} were identified in leaf, root, stem, respectively from the biomass collected from the area with the highest rare metal pollution, which was an enriched light mining area with EPR, consisting of 1224 mg kg^{-1} EER. Their article also showed that fern collected from an uncontaminated site containing 15 mg kg^{-1} EER could accumulate up to 1121 mg kg^{-1} EER in its leaves.

Conclusively, the higher number of EER in soil is reflected in the higher degree of EER in plants; however, high concentrations of EER could be enriched in pteridophyte (fern) species, even in those growing in unpolluted locations. These results are in full agreement with other investigations [42, 76].

4.8. Phytomining of nickel

Due to the widespread occurrence of nickel (Ni)-rich serpentine soils (containing minerals of the serpentine subgroup, especially antigorite, chrysotile, or white asbestos, commonly found in ultramafic rocks) and the large number of hyperaccumulating plant species of Ni, phytomining research has been initiated for Ni recovery [77]. Early field experiments focused on plants of the genus *Odontarrhena* (syn. Alyssum), especially *Odontarrhena muralis* (syn. *Alyssum murale*) and *Odontarrhena corsica* (syn. *Alyssum corsicum*) [55]. Subsequently, field studies were initiated in Albania [43]. *Alyssum* has around 150 annual, biannual and perennial species. Some have the shape of a shrub. The most cultivated is the one that forms tall bushes of 20-30 cm and is covered with light yellow, fragrant flowers. *Alyssum* leaves are small, with a linear or oval shape. The plant also produces small fruits.

Rosenkranz et al. (2019) demonstrated the feasibility of Ni phytomining on an Austrian serpentine soil [77]. Considering the experimental setup, *O. chalcidica* was superior to native *N. goesingensis* in terms of shoot biomass, Ni concentration and Ni yield. The data suggest that *O. chalcidica* is, in particular a suitable species for Ni phytomining on the Austrian serpentine soil. The authors propose that the long-term sustainability and impact of phytomining on Ni availability and soil quality, and thus the success of long-term Ni phytomining, should be the focus of future studies.

4.9. Phytomining of zinc and cadmium

The potential ability of *Sedum plumbizincicola* to extract Cd and Zn from contaminated soils was demonstrated in greenhouse and field experiments. A field study was conducted in a mining area in Chunan region, Zhejiang province, where soils contained important amounts of Cd (36–157 μg g $^{-1}$), Zn (1930–7250 μg g $^{-1}$), Cu (530–8340 μg g $^{-1}$), Pb (71–6940 μg g $^{-1}$) due to pollution from mine tailings and wastewater processing [78]. *Sedum plumbizincicola* was the predominant species in this area, and shoot Cd and Zn concentrations ranged from 574 to 1470 μg g $^{-1}$ and from 9020 to 14,600 μg g $^{-1}$, respectively. Furthermore, Cd concentrations in leaves were approximately twice as high as in stems. Zinc concentrations in leaves were somewhat higher than or equal to those in stems. In a hydroponic experiment, Cd and Zn concentrations were recorded in shoots (7010 and 18,400 μg g $^{-1}$, respectively) approximately seven times and five times higher than in roots (840 and 3000 μg g^{-1}, respectively) after exposure to 100 μM $CdSO_4$ and 600 μM $ZnSO_4$, respectively.

4.10. Advantages and limitations of phytomining

Phytomining technology has a number of unique features and advantages, among which the following can be mentioned:

- Offers the possibility of exploiting poor ores or/and soils polluted with metals, which would be uneconomical if conventional mining methods are applied. Phytomining provides a viable solution by utilizing plants to absorb metals from the soil, making it economically feasible to recover valuable metals from otherwise uneconomical sources.
- Phytomining is recognized as a "green" technology due to its minimal environmental impact compared to traditional mining practices. By relying on the natural processes of plant uptake and translocation, phytomining reduces the need for disruptive excavation, which can lead to habitat destruction, soil erosion, and water pollution. Additionally, phytomining can help remediate polluted soils by extracting heavy metals and improving soil quality.

Despite its advantages, phytomining also faces several limitations that must be addressed:

- Dependency on environmental factors: Phytomining is dependent on climate and season, as well as biogeochemical factors that influence plant activity, namely: rhizobiological activity, root exudates, temperature, humidity, pH and concentration of competing ions that affect plant growth rate and metal solubility and availability in soil [7]. This dependency on environmental conditions can pose challenges in maintaining consistent yields and productivity in phytomining operations.
- Limited metal uptake efficiency: The effectiveness of phytomining is contingent upon the ability of plants to absorb and accumulate metals from the soil. To interact with the metal, it must be in contact with the plant's root zone, which means that either the plants must be able to extend their roots, or the metal must be mobile to be within range of the plant's roots. However, not all plant species exhibit high metal uptake efficiency, and the availability of metals in the soil also plays a crucial role. Additionally, the mobility of metals in the soil and their accessibility to plant roots can impact the overall efficiency of metal extraction. The use of chelators (solubilizing agents) to increase metal mobility can also create problems if the amount of chemical applied is above the level of metal in the soil solution that could be efficiently taken up by plants [49].

Overall, while phytomining holds promise as a sustainable and environmentally friendly approach to metal extraction, addressing its limitations and optimizing operational practices will be essential for its widespread adoption and success in the mining industry.

Conclusions

Phytomining is a viable and important technology for the recovery of critical metals, particularly heavy metals like nickel. The process of phytomining involves the use of plants to absorb these metals from the soil, which can then be recovered from the plant matter.

Recovery of metals from high biomass plant crops grown in soil substrates, especially those associated with heavy metal pollution can be achieved by applying recent, more advanced phytoremediation technology to produce low-volume, sulphide-free 'bio-ore', which can be safely further processed if the target metal is of significant economic value. This technology also has potential applications in the mining industry for the recovery of heavy metals from poor ores.

Commercial metal mining is usually carried out from ores that have a high concentration of target metals, but requires huge capital investment and complex extraction processes. Sub-economic ores are more numerous and the metal content is well below the metal content required to be economically mined and processed by conventional techniques. Numerous lands around the globe are polluted with metals that could be phytomined. In recent years, major scientific advances have been made in understanding the potential application of this plant-based technique in the mining industry.

Plants provide several patterns of response to the presence of high metal concentrations in soil. Most are sensitive to high concentration of metals, especially if they are toxic, and others have developed resistance, tolerance and can bioaccumulate heavy metals in roots and aboveground parts such as shoot, flowers, stems and leaves. Plants suitable for phytomining are called hyperaccumulators because they accumulate large amounts of metals in their tissues and sap.

Phytomining has become more and more important in the conditions in which today's world is increasingly facing a crisis of raw materials, some of which are severely deficient, also called critical raw materials, among which some metals are also found. The development of the phytomining process is linked to the European initiative on raw materials launched by the European Commission in 2008.

Plants that can extract and absorb metals from polluted soils can be considered, first of all, as indicators of the presence of metals in the soil, but immediately the idea of their application in soil remediation arose. In a second stage, it was found that the metals present in the plant biomass can be recovered, through the phytomining technique. Therefore phytomining can fulfill two tasks: metal extraction, soil depollution.

The manuscript highlights the economic importance of phytomining, presenting case studies on the recovery of various critical metals. It also provides an analysis of the environmental and economic impacts of the phytomining process, using nickel as a specific example.

The manuscript identifies both the advantages and limitations of phytomining. On one hand, phytomining can contribute to the remediation of soil quality and the recovery of critical raw materials. On the other hand, the manuscript suggests that certain factors, such as the application of chelators, need to be carefully managed to avoid negative effects like metal immobilization.

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