



Review

# Soil Phytomining: Recent Developments—A Review

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**Abstract:** Phytomining (PM) is defined as the process of using plants capable of bio-extracting metals from soil in order to explore them economically. This relatively new, innovative method has been gathering significant attention in both the academic and commercial domains. Conventional mining methods are often economically unviable when applied to lean ores, and they can lead to secondary pollution in soil—a situation that applies to all excavated metals. On the other hand, PM is an environmentally friendly and economically viable solution that addresses the growing demands for metal resources, while simultaneously contributing to energy production by harnessing biomass energy. This comprehensive review presents the current PM techniques, challenges, and the hyperaccumulator plant species that may be used for the extraction of the main targeted elements in the process. Typically, the targeted metals are those of economic value, which can later be deposited or sold to various industries. This review also analyzes the factors influencing the economic viability of PM and proposes potential enhancements. Undeniably, PM offers the opportunity for economically sustainable exploration of metal-rich soils, but its full commercial viability remains constrained under current conditions as scientists are actively searching for the identification and utilization of new hyperaccumulator plant species in different locations worldwide, while creating new relationships and business avenues within the mining industry. Overall, this review highlights the current status of PM technology and the plants used, emphasizing the need for further research to enhance its commercial implementation and its potential to assist the mining industry. We conclude that PM, although a relatively new and unexplored concept, may provide economic and environmental benefits to soil end-users and managers who must cultivate on metal-contaminated soils as PM may turn yield shortages (of specific commercial crops) to benefits if high-yield hyperaccumulators are cultivated for industrial valorization of their high metal-content biomass.

**Keywords:** hyperaccumulators; metal-rich soils; biomass energy; environmental sustainability; economics of agromining



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## 1. Introduction

Phytoremediation is the process of remediating (or cleaning up) a soil elevated with pollutants with the use of plants (“phyto”). Many endemic plants, also known as metallophytes, can be found to be naturally grown in soils with elevated metal concentrations [1]. These unique plant species, also called “hyperaccumulators”, have portrayed natural tolerance to the presence of metals in soil or an enhanced ability for their accumulation. These plants might be genotypes that have evolved such tolerant characteristics due to their establishment in metalliferous areas for centuries or millennia [2]. The accumulation of metals in plants occurs in their root system or in the aerial biomass like stems, leaves, and flowers. According to Soleymanifar et al. [3], a plant capable of concentrating a metal significantly higher than a “regular” plant in its tissues when grown in the same area is characterized as a hyperaccumulator. Hyperaccumulators have the potential of absorbing metals from soil via their root system and translocating them into their aerial parts [4]. In this way, a contaminated soil may be phytoextracted. Thus, phytoextraction is the process of using

hyperaccumulator plants to absorb potentially toxic elements from soil with the aim of remediating the soil. A variation in phytoextraction is phytomining (PM). Phytomining is the process under which plants are used to extract (“mine”) valuable inorganic elements from soil in a natural or in an induced manner for the specific purpose of financial gain after valorizing the produced biomass. The difference between PM and phytoextraction is the valorization of the plant biomass; in the former case, it is solely dedicated to being used for recovering the metals for use in the metallurgical industry. In the latter, it can have any uses except from that—pharmaceutical, aromatic, energy, biochar, etc. Conventional mining is only performed in ore deposits where metal contents are highly enriched (i.e., soil concentrations are well above the maximum legal regulation limits). Nevertheless, these kinds of deposits are being depleted because of increased population and emerging needs, as well as rapid industrial and economic advancement [5]. Even though traditional mining methods are successful, they cannot recover all of the valuable metals. After the completion of the mining process, there is still about 3% to 10% of metals left in the soil [5]. These areas are characterized as “degraded” due to the fact that they contain lower concentrations of metals and minerals than what would be economically explorable [6]. Usually, such ore bodies are related to soils formed on ultramafic and serpentine parent materials. During the cool-down of ultramafic magma, minerals such as olivine and pyroxene, rich in magnesium (Mg) and iron (Fe), have a higher melting point and therefore crystallize at higher temperatures, leading to their dominance, along with some elements like nickel (Ni) and chromium (Cr), in ultramafic rocks. These types of soils are rich in various metals such as Mg, Fe, Ni, Cr, manganese (Mn), cobalt (Co), and titanium (Ti) [7,8].

In order to facilitate the phytoaccumulation, metals can be dissolved from the ore by applying strong acids or with the technique of electrorefining, in which metal ions gain electrons and form soil metal deposits at the electrode’s surface [9]. In this way, metals in soil may become more phytoavailable, and thus their uptake to hyperaccumulator plants may be increased and, in turn, PM may occur. Hence, instead of going through the usual procedures of soil excavation for mining, the extractions are performed with the use of hyperaccumulator plants.

The concept of metal accumulation in plants and PM was first introduced by Jaffré et al. [10]. To date, scientists also refer to the process as “agromining” [11], in order to encompass the entire agricultural system of ore–soil–plants. The whole process offers the opportunity to extract metals from sites where conventional mining methods are not economically viable. The environmental effect of the method is minimal due to the balance action of the plants opposing soil erosion caused by excavation [12]. This method offers a sustainable way to remediate or restore soil, while simultaneously recovering valuable metals from soil [13]. Conventional methods used to remediate and decontaminate polluted sites often result in secondary pollution, aggravating the environmental challenges. The presence of plants minimizes the spread of metals and reduces the risk of wind and water soil erosion. Moreover, in large-scale PM applications, there is the possibility to harness the energy stored within the harvested plant biomass [3].

The bioaccumulation factor (BAF) and translocation factor (TF) are used to determine the efficiency of metal uptake from soil to plant and metal translocation within the plant, respectively [14]. The BAF is an index obtained by dividing the concentration of a metal in the aerial parts of a plant by its concentration in the surrounding soil. This factor provides insights into the ability of the plant to absorb and accumulate metals from the soil. On the other hand, TF is the ratio of metal concentration in the aerial plant parts to that in the roots. Higher TF values indicate a greater ability to efficiently translocate metals from the roots to the above-ground parts of a plant [14]. To be classified as a hyperaccumulator, a plant must have both BAF and TF values exceeding 1.0, signifying a great ability to absorb metals from soil and translocate them upwards in the aerial parts [15]. These indicators can be influenced by the effect of metal concentration in the plant. Therefore, biomass production and metal availability in the soil or substrate must be taken into consideration.

The aim of this review was (a) to provide a comprehensive overview on the current PM status, including challenges associated with the method, (b) to analyze the economic viability of PM as an eco-friendly alternative to conventional mining, and (c) to discuss PM technology and the plants used, highlighting the importance of further research and development to enhance large scale implementation. We see this contribution as a highly necessary input so that essential knowledge and technological and scientific advancements may be updated and the community of scientists, interested stakeholders, and other soil end-users may benefit from the elucidation of mechanisms, processes, and practical considerations.

## 2. Elements Involved in Phytomining

### 2.1. Phytomining Elements

The elements of interest in the PM process are Ni, Co, cadmium (Cd), zinc (Zn), selenium (Se), Mn, thallium (Tl), and the noble metals (NMs). However, the majority of research efforts have focused on advancing the PM process of Ni [16]. For each metal, there is an established threshold that needs to be satisfied in order for a plant to be acknowledged as a hyperaccumulator. The selection of the limits is not entirely random but instead an indicator of a unique form of plant response, suggesting the presence of an unusual behavior. For instance, Sheoran et al. [5] suggested a limit of 1000 mg kg<sup>-1</sup> of dry plant weight (DW) for Ni, after tests conducted on *Homalium* and *Hybanthus* plants in different areas. Similarly, Baker and Brooks [17] set the limit to 10,000 mg kg<sup>-1</sup> DW for Mn and Zn after reporting high Zn concentrations in *Thlaspi calaminare* and *Viola calaminaria* leaves. Generally, over 700 plant species have been identified for their PM capabilities, most of which are Ni hyperaccumulators. The established limits for most of the elements that demonstrate an interest for being phytomined are shown in Table 1. When selecting plants for metal extraction, certain characteristics are important; these include three important features: high biomass yield, high Ni concentration in shoots (>1%), and fast growth [18]. The reason is that the phytoextracted amount of any given metal is equal to the concentration times biomass yield. All discussion is based on results obtained from field experiments, unless otherwise stated per particular case.

**Table 1.** Minimum threshold concentration of a metal in plants so that the species may be regarded as a hyperaccumulator. The accumulation refers to vegetative parts which can be harvested, most likely aerial biomass.

Element	Hyperaccumulation Threshold (mg kg <sup>-1</sup> )	Number of Hyperaccumulator Plant Species	Reference
Ag	1	-	Sheoran et al. [5]
Au	1	-	Sheoran et al. [5]
Cd	100	24	Van der Ent et al. [18]
Co	300	29	Krämer et al. [19]
Mn	10,000	22	Baker and Brooks [17]
Ni	1000	532	Soleymanifar et al. [3]
Se	100	20	Reeves [20]
Tl	100	1	Sheoran et al. [5]
Zn	3000	24	Van der Ent et al. [18]

The hyperaccumulation threshold was originally established as a metal concentration in plant shoots 10 to 100 times higher when compared to measurements in the shoots of “normal” plants under similar conditions. It was redefined by Van der Ent et al. [18], who suggested that the initial concentrations should be at least 10 times higher than the measurements obtained in plants on metalliferous soils, and 100 to 1000 times higher in plants

grown on regular soils (non-metal-enriched). Typically, most of the hyperaccumulating plant species are endemic to metalliferous soils. Since the root system of these plants is not usually collected during harvest, it is also mandatory for hyperaccumulators to exhibit BAF and TF values over 1, indicating that metals can be relocated in the upper part of the plant and recovered through combustion [14].

### 2.1.1. Nickel

As already mentioned, soils developed on ultramafic materials are expected to contain large amounts of Ni; hence, they are considered prime cases for Ni PM. Even though Ni in soil can be retained by Fe and Mn oxides, Ni hyperaccumulators can still accumulate a sufficient amount of the metal until the depletion of the source. According to Nkrumah et al. [16], 15–50 years are required before all easily accessible Ni is depleted. In addition, the physical properties of the soil are very important when it comes to PM. Well-drained soils are optimum for the cultivation of Ni hyperaccumulators, while soils that do not drain well may lead to decreased amount of plant biomass that is produced and, therefore, to a decreased amount of Ni that is extracted. For successful and economically viable Ni PM, soils should have an optimum content of moisture to maximize the amount of Ni absorbed by hyperaccumulator plants [21]. In the future, plant breeding techniques can make PM operations more profitable. Table 2 shows the main Ni hyperaccumulator plants that have great potential in Ni extraction from soils. Most of the plants that can hyperaccumulate Ni are species from approximately 40 different families, with the most important representatives being the Brassicaceae, Euphorbiaceae, Phyllanthaceae, Salicaceae, Buxaceae, and Rubiaceae family groups. Most of them are endemic plants found in soils derived from ultramafic rocks. The first report for Ni hyperaccumulation was made by Minguzzi and Vergnano [22], but the work was not widely recognized. Jaffré et al. [10] were the first to establish the term “phytomining” after noticing the accumulation of Ni in *Sebertia accuminata*, an endemic tree in forests of New Caledonia. Chaney et al. [23] were the first to conduct a field experiment for PM in the US Bureau mines in Reno, Nevada, where a Ni hyperaccumulator *Streptanthus polygaloides* was found to have bioaccumulated 10,000 mg kg<sup>-1</sup> DW in serpentine soils containing 3500 mg kg<sup>-1</sup> Ni. The second field trial was a two-year research study conducted by Robinson et al. [24], who extracted up to 8000 mg kg<sup>-1</sup> DW Ni and had 110,000 mg kg<sup>-1</sup> Ni in ash in *Alyssum bertolonii*. They also planted *Berkheya coddii*, which accumulated a total of 5500 mg kg<sup>-1</sup> DW. It was also reported that *B. coddii* was a very good candidate for Ni extraction due to its high biomass yield, perennial life cycle, and tolerance to abiotic stress [24].

Numerous research studies have reported elevated concentrations of Ni in plant tissues when grown in these types of soils. All Ni PM research has focused on plants that can accumulate amounts more than 1% (i.e., 10,000 mg kg<sup>-1</sup>) in their leaves and the harvested biomass, after collecting small plant samples (1 cm<sup>2</sup> or less) from serpentine soils in California. Indeed, Reeves et al. [25] found that *Streptanthus polygaloides* was able to accumulate Ni up to 1.5%, which led Mohsin et al. [26] to mention this plant as a good option for PM. Cole [27] reported the uptake of 5000 mg kg<sup>-1</sup> Ni in the dried leaves of *Hybanthus floribundus* in lateritic soils in Western Australia, where background levels were approximately 500 mg kg<sup>-1</sup> in the surface soil. In another study, Li et al. [7] reported a concentration of up to 22,000 mg kg<sup>-1</sup> that was absorbed by *Alyssum murale* and *Alussum corsicum* plants (Brassicaceae), grown in Ni-contaminated soils in a 120-day greenhouse experiment. In addition, plants were fertilized and the pH was adjusted. Recently, *Alyssum* hyperaccumulators have received wide interest regarding their phytoextraction potential [16]. Durand et al. [28] conducted a 7-month pot experiment using *Odontarrhena chalcidica* (syn. *Alyssum murale*) spiked with Ni sulfate. They reported increased metal availability as well as BAF and TF values.

**Table 2.** Ni hyperaccumulation plant species. The accumulation of the elements refers to vegetative plant parts which can be harvested and valorized for the contained metal.

Plant Species	Family	Ni Concentration (mg kg <sup>-1</sup> )/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	Reference
<i>Alyssum baldaccii</i>	Brassicaceae	1430–17,670	Ex situ; plant analysis; serpentine soils; Mediterranean climate; Mt. Smolikas, Greece	Bani et al. [29]
<i>Alyssum bertolonii</i>	Brassicaceae	4653–13,102/7–9	Hydroponics experiment; contained 400 mL Hoagland solution; plants spiked with NiSO <sub>4</sub> ; Italy	Galardi et al. [30]
<i>Alyssum bertolonii</i>	Brassicaceae	800/9	2-year field experiment; applied various amounts of NPK fertilizer; Mediterranean climate; Murlo, Italy	Robinson et al. [24]
<i>Alyssum chalcidicum</i>	Brassicaceae	1700	Ex situ; plant analysis; ultramafic rocks and hot springs; pseudo-total Ni concentration 1560 mg kg <sup>-1</sup> soil; Mediterranean climate; Euboea Island, Greece	Kanellopoulos and Argyraki [31]
<i>Alyssum euboicum</i>	Brassicaceae	26–4550	Ex situ; plant analysis; serpentine soils; Mediterranean climate; Turkey	Bani et al. [29]
<i>Alyssum heldreichii</i>	Brassicaceae	11,800	Ex situ; plant analysis; serpentine soils; pseudo-total Ni concentrations 1160 mg kg <sup>-1</sup> soil; Mediterranean climate; Katara pass, Greece	Bani et al. [29]
<i>Alyssum lesbiacum</i>	Brassicaceae	2900–22,400/4.2–10	Hydroponics experiment; applied nutrient solution; solution spiked with 0–250 μmol L <sup>-1</sup> NiSO <sub>4</sub> ; Greece	Adamidis et al. [32]
<i>Alyssum markgrafii</i>	Brassicaceae	<3–19,100	Ex situ; plant analysis; serpentine soils; pseudo-total Ni concentration in soil 1670 mg kg <sup>-1</sup> ; Mediterranean climate; Gjegjan; Albania	Bani et al. [29]
<i>Alyssum murale</i>	Brassicaceae	7–34,690/10.2–20	5-year field experiment; pseudo-total Ni concentration in soil 3180 mg kg <sup>-1</sup> ; fertilized with 100 kg ha <sup>-1</sup> N; Mediterranean climate; Pojska, Albania	Bani et al. [29]
<i>Berkeya coddii</i>	Asteraceae	40–5800	Pot experiment in glasshouses; plants spiked with 4–1000 mg Ni kg <sup>-1</sup> potting mix; New Zealand	Keeling et al. [33]
<i>Brackenridgea palustris</i>	Melastomataceae	1440/6.74	Ex situ; plant analysis; ultramafic rocks; pseudo- total Ni concentration—7051–10,521 mg kg <sup>-1</sup> ; Tropical climate; Sulawesi, Indonesia	Van der Ent et al. [34]
<i>Cloezia artensis</i>	Myrtaceae	35–1729	Field experiment; extractable Ni concentrations in soil—35–208 mg kg <sup>-1</sup> ; Semi-Tropical climate; New Caledonia	Becquer et al. [35]
<i>Codia spatulata</i>	Cunoniaceae	27–1420/6.5	Field experiment around mine sites; Semi-Tropical climate; New Caledonia	Jaffré et al. [36]

Table 2. Cont.

Plant Species	Family	Ni Concentration (mg kg <sup>-1</sup> )/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	Reference
<i>Dichapetalum gelonioides</i>	Dichapetalaceae	3160	Ex situ; plant analysis; ultramafic rocks; pseudo-total Ni concentrations—7051–10,251 mg kg <sup>-1</sup> soil; Tropical climate; Sulawesi, Indonesia	Van der Ent et al. [34]
<i>Geissois Pruinosa</i>	Cunoniaceae	3000–15,106/38.5	Field experiment around mine sites; Semi-tropical climate; New Caledonia	Jaffré et al. [36]
<i>Knema matanensis</i>	Myristicaceae	2500–5000	Ex situ; plant analysis; ultramafic rocks; pseudo total Ni concentrations—7051–10,251 mg kg <sup>-1</sup> soil; Tropical climate; Sulawesi, Indonesia	Van der Ent et al. [34]
<i>Miscanthus floridulus</i>	Poaceae	667–778	Ex situ; plant analysis; uranium tailings with background Ni concentration 11.5 mg kg <sup>-1</sup> soil; Tropical climate; South China	Li et al. [37]
<i>Myristica laurifolia</i>	Myristicaceae	1100	Ex situ; plant analysis; ultramafic rocks; pseudo-total Ni concentrations—7051–10,251 mg kg <sup>-1</sup> ; Tropical climate; Sulawesi, Indonesia	Van der Ent et al. [34]
<i>Peripterygia marginata</i>	Araliaceae	23–1800	Field experiment around mine sites; Semi-Tropical climate; New Caledonia	Jaffré et al. [36]
<i>Phyllanthus discolor</i>	Phyllanthaceae	13,670–31,490	Ex situ; plant analysis; ultramafic rocks; Tropical climate; Cuba	Berazain et al. [38]
<i>Phyllanthus orbicularis</i>	Phyllanthaceae	4140–10,950	Ex situ; plant analysis; ultramafic rocks; Tropical climate; Cuba	Berazain et al. [38]
<i>Phyllanthus xpallidus</i>	Phyllanthaceae	15,390–60,170	Ex situ; plant analysis; ultramafic rocks; Tropical climate; Cuba	Berazain et al. [38]
<i>Phyllantus insulae</i>	Phyllanthaceae	34,330–38,720	Ex situ analysis; ultramafic rocks; pseudo-total Ni concentrations—7051–10,251 mg kg <sup>-1</sup> ; Tropical climate; Sulawesi, Indonesia	Van der Ent et al. [34]
<i>Planchonella oxyhedra</i>	Sapotaceae	19,600/10	Ex situ; plant analysis; ultramafic rocks; pseudo-total Ni concentrations—7051–10,251 mg kg <sup>-1</sup> soil; Tropical climate; Sulawesi, Indonesia	Van der Ent et al. [34]
<i>Planchonella oxyhedra</i>	Sapotaceae	24,100–27,500/30–40	Ex situ; plant analysis; ultramafic rocks; Tropical climate; Halmahera Island, Indonesia	Hamdan et al. [39]
<i>Rinorea bengalensis</i>	Violaceae	20,000–25,100/30–40	Ex situ; plant analysis sampling; ultramafic rocks; Tropical climate; Halmahera Island, Indonesia	Hamdan et al. [39]
<i>Sarcotheca celebica</i>	Oxalidaceae	700–1000	Ex situ; plant analysis; ultramafic rocks; pseudo-total Ni concentrations—7051–10,251 mg kg <sup>-1</sup> soil; Tropical climate; Sulawesi, Indonesia	Van der Ent et al. [34]

Table 2. Cont.

Plant Species	Family	Ni Concentration (mg kg <sup>-1</sup> )/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	Reference
<i>Streptanthus polygaloides</i>	Brassicaceae	4000/21.4	Ex situ; plant analysis; serpentine soil; California, USA	Davis and Boyd [40]
<i>Thlaspi apterum</i>	Brassicaceae	16,600–21,500	Ex situ; plant analysis; serpentine soils; pseudo-total Ni concentrations 2858 mg kg <sup>-1</sup> soil; Mediterranean climate; Fotinovo, Bulgaria	Bani et al. [29]
<i>Thlaspi ochroleucum</i>	Brassicaceae	3400	Ex situ; plant analysis; serpentine soils; pseudo-total Ni concentrations 2770 mg kg <sup>-1</sup> soil; Mediterranean climate; Kardzali, Bulgaria	Bani et al. [29]
<i>Thlaspi tymphaeum</i>	Brassicaceae	7000	Ex situ; plant analysis; serpentine soils; pseudo-total Ni concentrations 2340 mg kg <sup>-1</sup> soil; Mediterranean climate; Malakasi, Greece	Bani et al. [29]
<i>Trichospermum kjelbergii</i>	Malvaceae	3770	Ex situ; plant analysis; ultramafic rocks; pseudo-total Ni concentrations—7051–10,251 mg kg <sup>-1</sup> soil; Tropical climate; Sulawesi, Indonesia	Van der Ent et al. [34]

### 2.1.2. Cobalt

The standard for plants to be classified as Co hyperaccumulators was set at 1000 mg kg<sup>-1</sup> by Baker and Brooks [17] until Krämer [19] revised it to 300 mg kg<sup>-1</sup>, reporting that the former accumulation of Co is rare. Normal amounts of Co in plants are well below 0.1 mg kg<sup>-1</sup>. Even in soils characterized with elevated amounts of Co, such as those deriving from ultramafic rocks, the amount of Co in plants rarely surpasses 20 mg kg<sup>-1</sup>. It seems that the presence of Ni in such soils interferes with Co accumulation. For instance, as mentioned before, *Berkheya coddii* is also a Ni hyperaccumulator. The presence of Co can inhibit the absorption of Ni when these metals are both present in the medium, leading to PM limitations. Keeling et al. [33] reported that Co can be absorbed by *B. coddii* plants with or without the presence of Ni in the growing medium (50% peat and 50% pumice). On the other hand, increased Co concentrations in soil from 125 up to 1000 mg kg<sup>-1</sup> significantly decreased the harvested biomass due to plant toxicity, although the plant's BAF was not affected. In trials where only Ni (at 1000 mg kg<sup>-1</sup>) or only Co (at 4–1000 mg kg<sup>-1</sup>) were present in soil, the crop yielded approximately 14.5 kg ha<sup>-1</sup> (when for Ni) and 12.6 kg ha<sup>-1</sup> (for Co). On the other hand, when Co and Ni were both present in soil (with concentrations of Ni = 500 and Co = 500 mg kg<sup>-1</sup>), the metal yield significantly dropped to 0.9 kg of Ni ha<sup>-1</sup> and 3.9 kg of Co ha<sup>-1</sup>, and this indicates that PM may be limited due to interference of each other's absorption by the plant. Similar to this, Rue et al. [41] suggested that *B. coddii* could be utilized in areas with high concentrations of Co but low Ni after testing the plant in pot experiments. Specifically, they found that the Co concentration reached 1980 mg kg<sup>-1</sup> when treated with 10 mg kg<sup>-1</sup> Ni (as Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and 100 mg kg<sup>-1</sup> Co (as Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), while total biomass can reach up to 22 t ha<sup>-1</sup>, which could yield 16.3 t Co ha<sup>-1</sup>. Similar findings were reported by Parks [42], who noticed the competitive role between Ni and Co accumulation in *Rinorea bengalensis*. However, *R. bengalensis* was found to be tolerant to Ni and managed to accumulate a concentration of 1200 mg Co kg<sup>-1</sup> when grown on ultramafic rocks. Both Ni and Co were added as Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O at 750 mg kg<sup>-1</sup>, respectively. An exceptional ability for Co PM was shown after collecting leaf samples of *Nyssa sylvatica* var. *biflora* and var. *sylvatica* (Nyssaceae) grown on ultramafic rocks in New Caledonia, which were found to accumulate up to 845 mg Co kg<sup>-1</sup> [43]. The same was

reported for the well-known Ni hyperaccumulator *Alyssum murale*, which accumulated 1320 mg Co kg<sup>-1</sup> DW when grown in sandy loam soils (<2 mg Co kg<sup>-1</sup> dry soil) spiked with 59.8 mg (1 mmol) Co kg<sup>-1</sup> dry soil [44].

The addition of elemental zero-valent sulfur in soil can help increase the amount of metal that plants can absorb. According to Robinson et al. [45], sulfur content in soil at a rate of 5000 mg kg<sup>-1</sup> increased the amount of Co that was absorbed by *Berkheya coddii* plants to 299 mg kg<sup>-1</sup> DW, 5 times greater than the control treatment (56 mg kg<sup>-1</sup> DW). Hence, this is especially beneficial in soils that do contain some amount of metals but not enough for the plants to take up the maximum quantity they need. In addition, sulfur is a cost-benefit additive, compared to EDTA, ethylenediaminetetraacetic acid, a synthetic molecule frequently used to increase metal mobility and soil, for enhancing the growth of metal-rich plants in soils with low metal concentrations. Overall, plant species that have demonstrated Co hyperaccumulation are shown in Table 3.

**Table 3.** List of all Co hyperaccumulators. Concentrations in plants refer to leaves unless otherwise stated.

Plant Species	Family	Co (mg kg <sup>-1</sup> DW)/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	References
<i>Acalypha cupricola</i>	Euphorbiaceae	207–904	Ex situ; plant analysis; samples from Co/Cu mine sites; Equatorial climate; Katanga, Congo	Faucon et al. [46]
<i>Aeollanthus subacaulis</i>	Lamiaceae	0–1900	Pot experiment (200 g sterilized soil); soil containing 10,000 mg Co kg <sup>-1</sup> as nitrate; Congo	Morisson et al. [47]
<i>Alectra sessiliflora</i>	Orobanchaceae	21–866	Ex situ; plant analysis; samples collected from Co/Cu mine sites; Equatorial climate; Katanga, Congo	Faucon et al. [46]
<i>Alyssum corsicum</i>	Brassicaceae	1080 (shoot)/4.2–10	Field experiment in various soil types; 150 kg N ha <sup>-1</sup> , 100 kg P ha <sup>-1</sup> , and 75 kg K ha <sup>-1</sup> were applied; Beltsville, USA	Malik et al. [44]
<i>Alyssum heldreichii</i>	Brassicaceae	1000	Pot experiment; plants spiked with different concentrations of metals; New Zealand	Homer et al. [48]
<i>Alyssum murale</i>	Brassicaceae	2070 (shoot)/10.2–20	Field experiment in various soil types; 150 kg N ha <sup>-1</sup> , 100 kg P ha <sup>-1</sup> , and 75 kg K ha <sup>-1</sup> were applied; Beltsville, USA	Malik et al. [44]
<i>Alyssum pintodasilvae</i>	Brassicaceae	1000	Pot experiment; plants spiked with different concentrations of metals; New Zealand	Homer et al. [48]
<i>Alyssum tenium</i>	Brassicaceae	1000	Pot experiment; plants spiked with different concentrations of metals; New Zealand	Homer et al. [48]
<i>Alyssum troodii</i>	Brassicaceae	10–2325	Pot experiment; plants spiked with different concentrations of metals; Cyprus	Lange et al. [49]
<i>Anisopappus chinensis</i>	Asteraceae	3–1300	Ex situ; leaf analysis; Equatorial climate; Congo	Lange et al. [49]
<i>Aporosa chalarocarpa</i>	Phyllanthaceae	468	Ex situ; leaf analysis; samples collected from ultramafic rocks; Tropical climate; Sabah, Malaysia	Lange et al. [49]

Table 3. Cont.

Plant Species	Family	Co (mg kg <sup>-1</sup> DW)/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	References
<i>Berkeya coddii</i>	Asteraceae	40–2116/4.96–9.30	Experiment in controlled climate glasshouses; plants spiked with 4–500 mg Co kg <sup>-1</sup> ; New Zealand	Keeling et al. [33] Rue et al. [41]
<i>Buchnera henriquesii</i>	Orobanchaceae	404–930	Ex situ; plant analysis; plant samples collected from Co/Cu mine sites; Equatorial climate; Katanga, Congo	Faucon et al. [46]
<i>Celosia trigyna</i> L.	Amaranthaceae	75–501/9.5	Ex situ; plant analysis; plant samples collected from Co/Cu mine sites; Equatorial climate; Katanga, Congo	Olawuyi et al. [50]
<i>Crepidorhopalon perennis</i>	Linderniaceae	61–1105/0.32	Ex situ; plant analysis; plant samples collected from Co/Cu mine sites; Equatorial climate; Katanga, Congo	Faucon et al. [46]
<i>Crepidorhopalon tenuis</i>	Linderniaceae	8–605/0.16–0.32	Ex situ; plant analysis; plant samples collected from Co/Cu mine sites; Equatorial climate; Katanga, Congo	Faucon et al. [46]
<i>Lemna minor</i> L.	Araceae	5000	Pre-cultivated under laboratory conditions; fertilized with Hoagland solution; plants spiked with 0–200 µM CoCl <sub>2</sub> ·6H <sub>2</sub> O; Nanjing, China	Hu et al. [51]
<i>Glochidion cf. sericeum</i>	Phyllanthaceae	442–1310	Ex situ; leaf analysis; leaf samples collected from ultramafic rocks; Tropical climate; Sabah, Malaysia	Lange et al. [49]
<i>Haumaniastrum katangense</i>	Lamiaceae	864	Ex situ; leaf analysis; leaf samples collected from Cu/Co-Zn/Cu mine sites; background Co levels 1.2–85 mg kg <sup>-1</sup> ; Congo	Van der Ent et al. [52]
<i>Haumaniastrum robertii</i>	Lamiaceae	6160/20	Ex situ; leaf analysis; leaf samples collected from Cu/Co-Zn/Cu mine sites; background Co levels 1.2–85 mg kg <sup>-1</sup> ; Congo	Lange et al. [49]
<i>Hibiscus rhodanthus</i>	Malvaceae	42–274/0.054–1.6	Ex situ; plant analysis; Sub-tropical climate; Nyika Plateau, Zambia and Mozambique	Medwecka [53]
<i>Nyssa sylvatica</i> var. <i>biflora</i>	Nyssaceae	0–438/6	Ex situ; plant analysis; plant samples from granite derivatives; available Co content in soil—2.5%; Inabu-cho, Japan	Memon and Yatazawa [54]
<i>Nyssa sylvatica</i> var. <i>sylvatica</i>	Nyssaceae	800/6	Ex situ; plant analysis; South Carolina, USA	Busbee et al. [55]
<i>Rinorea bengalensis</i>	Violaceae	0.5–1200/30–40	Ex situ; leaf analysis; ultramafic rocks; Tropical climate; Halmahera Island, Indonesia	Hamdan et al. [39]

Table 3. Cont.

Plant Species	Family	Co (mg kg <sup>-1</sup> DW)/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	References
<i>Rinorea javanica</i>	Violaceae	3–670/30–40	Ex situ; leaf analysis; leaf samples collected from ultramafic rocks; Tropical climate; Halmahera Island, Indonesia	Hamdan et al. [39]
<i>Triumfetta welwitschii</i>	Malvaceae	162–1971	Ex situ; plant analysis; plant samples collected from Co/Cu mine sites; Equatorial climate; Katanga, Congo	Faucon et al. [46]
<i>Vernoniastrum latifolium</i>	Asteraceae	82–549	Ex situ; plant analysis; Equatorial climate; Congo	Lange et al. [49]
<i>Vigna dolomitica</i>	Fabaceae	241–540	Ex situ; plant analysis; Equatorial climate; Congo	Lange et al. [49]

### 2.1.3. Cadmium

Higher concentrations of cadmium (Cd), ranging from 10 to 200 mg kg<sup>-1</sup>, can be found in soils that have been exposed to waste materials due to Zn mining. In addition, such elevated Cd levels may also arise in soils that have received industrial waste or phosphate fertilizers enriched with Cd [7]. Natural levels of Cd in plants are usually less than 0.1 mg kg<sup>-1</sup>, but in Cd-contaminated soils these levels can exceed 20 mg kg<sup>-1</sup>. The cadmium established threshold in plants is defined as having a concentration of higher than 100 mg kg<sup>-1</sup>, as proposed by Van der Ent et al. [18]. However, in certain Zn-Pb mines, *Noccaea* species, such as *N. caerulescens* and *N. praecox*, have been found to contain Cd concentrations exceeding 100 mg kg<sup>-1</sup>, or even higher than 1000 mg kg<sup>-1</sup>. Shoots of *N. caerulescens* can easily contain over 2000 mg Cd kg<sup>-1</sup>, even when grown on contaminated soils, and over 20,000 mg kg<sup>-1</sup> when tested in nutrient solutions [56]. Other plants like *Impatiens walleriana*, *Pteris vittata*, *Sedum alfredii*, and *Thlaspi caerulescens* are capable of removing from soil 1168, 6434, 922.6, and 7400 mg kg<sup>-1</sup> of Cd, respectively [57]. Specifically, Nedelkoska et al. [58] treated the roots of *T. caerulescens* with a H<sup>+</sup>-ATPase inhibitor and measured a concentration of 62,800 mg Cd kg<sup>-1</sup> DW (6.3%) in the hair roots of the plant, which was grown in nutrient medium amended with a Cd concentration of 3710 ppm. On the other hand, there are significant variations among sites and within these plants [59]. Similar findings have been reported for *Arabidopsis halleri* by Bert et al. [60] and *Viola baoshanensis* by Deng et al. [61]. Specifically, *A. halleri* has been reported for its great ability to grow in different environments and its capability to store high amounts of Cd, especially when grown in polluted soils. According to Claire-Lise and Nathalie [62], *A. halleri* was able to accumulate up to 157 mg kg<sup>-1</sup> leaf dry weight when treated with 5 μM Cd or more. Also, it has been used as a plant model on metal tolerance and accumulation for identifying the genes involved. However, it has not been further tested due to the fact that it produces low biomass. Nevertheless, it was noted that for a plant to be considered as a Cd hyperaccumulator, it needs to be naturally grown in an area and sustain itself without human intervention [18]. The list of Cd hyperaccumulating species are shown in Table 4.

### 2.1.4. Zinc

As for Zn, it was found that *Thlaspi alpestre* var. *calaminare* (nowadays classified as *Noccaea caerulescens*) contained a minimum of 1% Zn in the dry leaf biomass [89]. Raschio [90] observed another Zn hyperaccumulator, *Thlaspi rotundifolium* ssp. *Cepaeifolium*, while Reeves and Brooks [91] proved that the *Thlaspi* genus consists of many Zn hyperaccumulators, with accumulated concentrations surpassing 1000 mg kg<sup>-1</sup> after experiments in mine tailings in Northern Italy. Baker et al. [92] showed that *T. caerulescens*, when

grown in nutrient-rich soils, could accumulate high concentrations of Zn, Cd, Co, Mn, and Ni. There were even instances where Zn accumulation reached the threshold of 10,000 mg kg<sup>-1</sup> [17] or surpassed it, which was initially considered as the established limit to characterize a plant as a Zn hyperaccumulator. Furthermore, Brown et al. [93] added 10,000 µM Zn and 200 µM Cd in a nutrient solution and caused an accumulation of 33,600 mg Zn kg<sup>-1</sup> in *T. caerulea*. Also *A. halleri*, after being tested in a hydroponics experiment treated with 1 µM and 1000 µM Zn, managed to accumulate Zn in the shoots 300 mg kg<sup>-1</sup> and 32,000 mg kg<sup>-1</sup>, respectively [94]. Also, in a hydroponics experiment conducted in China using *Potentilla griffithii*, it was shown that the plant was able to accumulate up to 11,400 mg Zn kg<sup>-1</sup> leaf dry weight after being treated with 160 mg Zn L<sup>-1</sup> [95]. However, the threshold of 10,000 mg kg<sup>-1</sup> was later revised to 3000 mg kg<sup>-1</sup> by Van der Ent et al. [18]. Also, Grimm [96] reported an accumulation of up to 11,700 mg kg<sup>-1</sup> in stems of *Brassica juncea*, when the soil concentration of Zn was only 330 mg kg<sup>-1</sup>. The list of all Zn hyperaccumulator plant species is shown in Table 5.

**Table 4.** List of Cd hyperaccumulating plant species.

Plant Species	Family	Achieved Concentration (mg kg <sup>-1</sup> )/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	References
<i>Arabidopsis halleri</i>	Brassicaceae	117.2	Pot experiment; nutrient solution applied as fertilizer; plants exposed to 0–100 µM CdSO <sub>4</sub> ; Blankerode, Germany	Zhao et al. [63]
<i>Arabis paniculata</i>	Brassicaceae	457	Hydroponics experiment; Hoagland solution applied as fertilizer; plants spiked with 0–267 µM CdCl <sub>2</sub> ·2.5H <sub>2</sub> O; Yunnan Province, China	Tang et al. [64]
<i>Bidens pilosa</i>	Asteraceae	400.7/5–6.7	Field experiment with total Cd concentration in soil 19.63 mg kg <sup>-1</sup> ; (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> and Ca(NO <sub>3</sub> ) <sub>2</sub> were added at 200 mg kg <sup>-1</sup> as fertilizers; Shaanxi, China	Dai et al. [65]
<i>Centela asiatica</i>	Apiaceae	105	Field and laboratory experiment; field pseudo-total Cd concentration—124–1000 mg kg <sup>-1</sup> , plants were spiked at levels 0–5 mg L <sup>-1</sup> in lab; South China	Liu et al. [66]
<i>Viola baoshanensis</i>	Cyperaceae	1168	Field survey and greenhouse experiment; nutrient solution was applied as fertilizer; plants spiked with 0–30 mg L <sup>-1</sup> ; Humid sub-tropical climate; Hunan Province, China	Liu et al. [67]
<i>Elodea canadensis</i>	Hydrocharitaceae	300	Hydroponics experiment; plants exposed to 0–0.5 µM CdCl <sub>2</sub> ; Stockholm, Sweden	Ali et al. [57] Nyquist and Greger [68]
<i>Helianthus annuus</i>	Helianthoideae	230/4.5	Pot experiment; background total Cd concentration in soil—30 mg kg <sup>-1</sup> ; pot spiked with 0–500 mg Cd L <sup>-1</sup> solution; Tropical climate; Korea	Lee et al. [69]

Table 4. Cont.

Plant Species	Family	Achieved Concentration (mg kg <sup>-1</sup> )/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	References
<i>Impatiens walleriana</i>	Balsaminaceae	1168	Pot experiment; containing total Cd—0.61 mg kg <sup>-1</sup> ; soil spiked with 20, 40, and 80 mg Cd(NO <sub>3</sub> ) kg <sup>-1</sup> ; China	Wei et al. [70]
<i>Ipomoea aquatica</i>	Convolvulaceae	138/7–30	Hydroponics experiment; nutrient solution containing 1 M of HNO <sub>3</sub> , H <sub>3</sub> PO <sub>4</sub> , and H <sub>2</sub> SO <sub>4</sub> was added; Beijing, China	Wang et al. [71]
<i>Lonicera japonica</i>	Caprifoliaceae	470.25/2.1–3.8	Hydroponics experiment; plant samples were collected from uncontaminated site; Hoagland solution was applied as fertilizer; plants were spiked with 0–50 mg CdCl <sub>2</sub> ·2.5H <sub>2</sub> O L <sup>-1</sup> ; China	Liu et al. [72]
<i>Siegesbeckia orientalis</i> L.	Asteraceae	192.92–6762	Field experiment and pot experiment; total Cd concentration 28.44 and 150 mg kg <sup>-1</sup> in soil and pots respectively; Huidong, China	Zhang et al. [73]
<i>Panicum virgatum</i>	Poaceae	280/18	Field experiment; N-fertilization ranged from 0–240 kg ha <sup>-1</sup> ; Mediterranean climate; Thessaly, Greece	Giannoulis et al. [74]
<i>Phytolacca americana</i>	Phytolaccaceae	42–637.7/0.53	Field experiment and hydroponic experiment; pseudo-total concentration in soil 1–1000 mg kg <sup>-1</sup> , plants spiked with 0–100 µM CdCl <sub>2</sub> ; Hoagland solution applied as fertilizer; China	Liu et al. [66]
<i>Potentilla griffithi</i>	Rosaceae	174	Field experiment; contaminated soil contained a total of 331 mg Cd kg <sup>-1</sup> ; Monsoon climate; Lanping, China	Hu et al. [51]
<i>Populus nigra</i>	Salicaceae	96.8/82	Hydroponics experiment; plant cuttings were exposed to 0–20 µM CdSO <sub>4</sub> ; Rome, Italy	Marmiroli et al. [75] Stolarski et al. [76]
<i>Picris divaricata</i>	Asteraceae	1343	Pot experiment with contaminated soil; total Cd amount in soil—15 mg kg <sup>-1</sup> ; Monsoon climate; Lanping, China	Tang et al. [77]
<i>Raphanus sativus</i>	Brassicaceae	326.75/33–42	Hydroponics experiment; 400 µmol L <sup>-1</sup> CaCl <sub>2</sub> was added; Korea, and Jiangxi, China	Kim and Hong [78] Chen et al. [79]
<i>Ricinus communis</i>	Euphorbiaceae	288/2–2.6	Ex situ; plant analysis; plant sampling from Cd contaminated sites; Cd concentration on soil—2.8 mg kg <sup>-1</sup> ; Subtropical climate; Zhejiang, China	Koutroubas et al. [80] Huang et al. [81]
<i>Salix viminalis</i>	Salicaceae	200/12	Hydroponics experiment; plant material spiked at 0, 10, 50, 200 µM CdCl <sub>2</sub> ; Birmensdorf, Switzerland	Stolarski et al. [76] Vollenweider et al. [82]

Table 4. Cont.

Plant Species	Family	Achieved Concentration (mg kg <sup>-1</sup> )/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	References
<i>Sedum alfredii</i>	Crassulaceae	6500–9000	Greenhouse experiment in pots; nutrient solution was applied; plants were treated with 12.5–800 μmol Cd L <sup>-1</sup> ; Quzhou, China	Yang et al. [83]
<i>Solanum nigrum</i> L.	Solanaceae	307–3163	Pot experiment; soil in pots spiked with various Cd concentrations (as CdCl <sub>2</sub> ) up to 80 mg kg <sup>-1</sup> ; Daegu, Korea	Khan et al. [84]
<i>Tagetes patula</i>	Asteraceae	324/26.8	Pot experiment; containing total Cd—0.61 mg kg <sup>-1</sup> ; soil spiked with 20, 40, and 80 mg Cd(NO <sub>3</sub> ) kg <sup>-1</sup> ; China	Marotti et al. [85] Wei et al. [70]
<i>Thlaspi caerulescens</i>	Brassicaceae	380–7400/1.6	Pot experiment containing contaminated soil—total Cd 20.3 mg kg <sup>-1</sup> ; fertilized with 13 mg N, 33 mg P, and 41 mg K kg <sup>-1</sup> soil; Northern France	Martínez et al. [86]; Perronnet et al. [87]
<i>Wolffia globosa</i>	Araceae	500/0.08	Hydroponics experiment in greenhouse; Hoagland solution applied as fertilizer; solution spiked at 0–100 μM Cd(NO <sub>3</sub> ); China	Xie et al. [88]

Table 5. Zn hyperaccumulating plant species.

Plant Species	Family	Achieved Concentrations (%) (Aerial Parts Are Specified)/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	References
<i>Anthyllis vulneraria</i>	Fabaceae	>1% (leaf)/0.1–0.4	Ex situ; plant analysis; plant samples were assisted by symbiotic bacteria; spiked with 0–35 mM ZnSO <sub>4</sub> ; Saint-Laurent-Le-Minier, France	Grison et al. [97]
<i>Arabidopsis halleri</i>	Brassicaceae	>1% (leaf)	Pot experiment; nutrient solution applied as fertilizer; plants exposed to 0–100 μM ZnSO <sub>4</sub> ; Blankerode, Germany	Zhao et al. [94] Peer et al. [98]
<i>Arabis paniculata</i>	Brassicaceae	>2% (leaf)	Hydroponics experiment; Hoagland solution applied as fertilizer; plants spiked with 0–2447 μM ZnSO <sub>4</sub> ·7H <sub>2</sub> O; Yunnan Province, China	Reeves et al. [99]; Tang et al. [64]

Table 5. Cont.

Plant Species	Family	Achieved Concentrations (%) (Aerial Parts Are Specified)/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	References
<i>Corydalis davidii</i>	Papaveraceae	>1% (leaf)	Field study and hydroponics experiment; total Zn in soil—9847 mg kg <sup>-1</sup> ; plants spiked with 50–400 mg Zn(NO <sub>3</sub> ) <sub>2</sub> L <sup>-1</sup> in hydroponic experiment; Sub-tropical climate; Magu, China	Balafrej et al. [100]; Lin et al. [101]
<i>Haumaniastrum katangense</i>	Lamiaceae	1.98% (shoot)/20	Field study, in situ leaf samples; Zair	Balafrej et al. [100]
<i>Noccaea alpestre</i>	Brassicaceae	>1% (leaf)	Ex situ; plant analysis; total Zn in soil 1900–35,000 mg kg <sup>-1</sup> ; Derbyshire, England	Shimwell and Laurie [102]
<i>Noccaea brachypetalum</i>	Brassicaceae	2% (shoot)	Field study, in situ leaf samples; Paris, France	Reeves and Brooks [103]
<i>Noccaea bulbosum Spruner</i>	Brassicaceae	1.05% (shoot)	Field study, in situ leaf samples; Mediterranean climate; Athens, Greece	Reeves and Brooks [103]
<i>Noccaea caerulescens</i>	Brassicaceae	2.73% (leaf)/1.6	Field study, in situ leaf samples; Temperate climate; Belgium	Martínez et al. [85] Reeves and Brooks [103]
<i>Noccaea calaminare</i>	Brassicaceae	3.96% (leaf)	Field study, in situ leaf samples; Temperate climate; München, Germany	Reeves et al. [99] Reeves and Brooks [103]
<i>Noccaea cepaeifolium</i>	Brassicaceae	2.10% (shoot)	Field study; total Zn concentration in soil—17,300 mg kg <sup>-1</sup> ; Mediterranean climate; Northern Italy	Reeves and Brooks [103]
<i>Noccaea eburneosa</i>	Brassicaceae	1.05% (shoot)	Field study, in situ leaf samples; Temperate climate; Zurich, Switzerland	Balafrej et al. [100] Reeves and Brooks [103]
<i>Noccaea limosellifolium</i>	Brassicaceae	1.10% (shoot)	Field study, in situ leaf samples; Paris, France	Reeves and Brooks [103]
<i>Noccaea praecox</i>	Brassicaceae	2.10% (leaf)	Field study, in situ leaf samples; Mediterranean climate; Bulgaria	Reeves and Brooks [103]
<i>Noccaea stenopterum</i>	Brassicaceae	1.60% (leaf)	Field study, in situ leaf samples; Temperate climate; Spain	Reeves and Brooks [103]
<i>Sedum alfredii</i>	Crassulaceae	0.45–1.9% (shoot)	Field survey and greenhouse experiment; plants exposed to 5–320 mg Zn L <sup>-1</sup> (as ZnSO <sub>4</sub> ·7H <sub>2</sub> O); Sub-tropical humid climate; Zhejiang Province, China	Yang et al. [104]
<i>Pieris divaricata</i>	Ericaceae	>6% (shoot)	Pot experiment with contaminated soil; total Zn amount in soil—352 mg kg <sup>-1</sup> ; Sub-tropical climate; Lanping, China	Balafrej et al. [100]

Table 5. Cont.

Plant Species	Family	Achieved Concentrations (%) (Aerial Parts Are Specified)/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	References
<i>Potentilla griffithii</i>	Rosaceae	>2.2% (leaf)	Field survey and hydroponics experiment; Hoagland solution was added as fertilizer; plants spiked with ZnSO <sub>4</sub> ·7H <sub>2</sub> O at 20–320 mg L <sup>-1</sup> ; Yunnan Province; China	Reeves et al. [99] Qiu et al. [105]
<i>Sedum plumbizincicola</i>	Crassulaceae	0.45–1.9% (shoot)	Field survey and greenhouse experiment; plants exposed to 5–320 mg Zn L <sup>-1</sup> (as ZnSO <sub>4</sub> ·7H <sub>2</sub> O); Sub-tropical humid climate; Zhejiang Province, China	Reeves et al. [99] Yang et al. [104]
<i>Viola baoshanensis</i>	Violaceae	>0.9%	Field survey and greenhouse experiment; modified Hoagland solution was applied as fertilizer; plants spiked with 0–130 mg ZnSO <sub>4</sub> ·7H <sub>2</sub> O L <sup>-1</sup> ; Humid sub-tropical climate; Hunan Province, China	Balafrej et al. [100]; Wu et al. [106]

### 2.1.5. Manganese

Manganese is a major trace nutrient with an expected concentration in plants grown in normal soil of ca. 40–50 mg kg<sup>-1</sup> and usual soil pseudo-total concentrations ca. 500–600 mg kg<sup>-1</sup>. However, in Mn-rich soils, Mn hyperaccumulator plants may accumulate 2 or even 3 orders of magnitude higher Mn concentrations. Research conducted by Jaffré [36,106] reported that 98 out of 450 of the plant species growing on soils developed on ultramafic rocks in New Caledonia with background Mn concentrations of 1000–5000 mg kg<sup>-1</sup> had average Mn concentrations above 1000 mg kg<sup>-1</sup>, while six species among them surpassed even 10,000 mg kg<sup>-1</sup>. Based on these findings, Baker and Brooks [17] decided to establish a threshold of 10,000 mg kg<sup>-1</sup> to define Mn hyperaccumulation. To date, there are 22 species that are known as Mn hyperaccumulators and these are listed in Table 6. In fact, due to exceptionally high levels of Mn, in some cases reaching a concentration of 2–5% of plant DW, the ash of these plants can contain as much as 10–25% Mn.

Table 6. List of Mn hyperaccumulator species.

Plant Species	Family	Achieved Concentration (mg kg <sup>-1</sup> )/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	Reference
<i>Alyxia poyaensis</i>	Apocynaceae	1.4%	Ex situ; plant analysis; Semi-tropical climate; New Caledonia	Losfeld et al. [107]
<i>Beaupreopsis paniculata</i>	Urticaceae	1.2%	Ex situ; plant analysis; Semi-tropical climate; New Caledonia	Jaffré [108]
<i>Chengiopanax sciadophylloides</i>	Araliaceae	2.4%	7-month field trial; exchangeable Mn in soil—931 mg kg <sup>-1</sup> ; Mie, Japan	Mizuno et al. [109]

Table 6. Cont.

Plant Species	Family	Achieved Concentration (mg kg <sup>-1</sup> )/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	Reference
<i>Denhamia cunninghamii</i>	Sapindaceae	2.5%	Ex situ; plant analysis; Queensland, Australia	Fernando et al. [110]; Fernando et al. [111]
<i>Denhamia silvestris</i>	Sapindaceae	1.2%	Pot experiment; medium spiked with soluble Mn <sup>2+</sup> at 0, 250, 500, and 1000 mg kg <sup>-1</sup> ; Queensland, Australia	Abubakari et al. [112]
<i>Denhamia fournieri</i>	Sapindaceae	2.0%	Ex situ; plant analysis; Semi-tropical climate; New Caledonia	Fernando et al. [110];
<i>Celosia argentea</i>	Sapindaceae	3.3%	Field survey and hydroponics experiment; Hoagland solution applied as fertilizer; plants exposed to 2.5–600 mg Mn L <sup>-1</sup> ; Guangxi Province, China	Jaffré [36] Liu et al. [113]
<i>Garcinia amplexicaulis</i>	Clusiaceae	1.2%/280	Ex situ; plant analysis; Semi-tropical climate; New Caledonia	Jaffré [36]
<i>Gossia bamagensis</i>	Myrtaceae	4.0%	Ex situ; leaf analysis; Queensland, Australia	Fernando et al. [110]; Fernando et al. [111]
<i>Gossia bidwillii</i>	Myrtaceae	1.9% (leaf), 2.6% (bark)	Ex situ; plant analysis; Sub-tropical climate; Brisbane, Australia	Losfeld et al. [107]; Bidwell et al. [114]
<i>Gossia clusioides</i>	Myrtaceae	1.0%	Ex situ; plant analysis; Semi-tropical climate; New Caledonia	Jaffré [36]
<i>Gossia diversifolia</i>	Myrtaceae	1.8%	Ex situ; plant analysis; Semi-tropical climate; New Caledonia	Losfeld et al. [107]
<i>Gossia fragrantissima</i>	Myrtaceae	3.5%	Ex situ; leaf analysis; Queensland, Australia	Fernando et al. [110] Fernando et al. [111]
<i>Gossia gonoclada</i>	Myrtaceae	1.5%	Ex situ; leaf analysis; Queensland, Australia	Fernando et al. [110]; Fernando et al. [111]
<i>Gossia lucida</i>	Myrtaceae	1.5%	Ex situ; leaf analysis; Queensland, Australia	Fernando et al. [110] Fernando et al. [111]
<i>Gossia sankowskiorum</i>	Myrtaceae	3.0%	Ex situ; leaf analysis; Queensland, Australia	Fernando et al. [110] Fernando et al. [111]
<i>Gossia shepherdii</i>	Myrtaceae	1.5%	Ex situ; leaf analysis; Queensland, Australia	Fernando et al. [110] Fernando et al. [111]
<i>Phytolacca americama</i>	Proteaceae	1.1%	Ex situ; analysis; Semi-tropical climate; New Caledonia	Jaffré [108]

Table 6. Cont.

Plant Species	Family	Achieved Concentration (mg kg <sup>-1</sup> )/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	Reference
<i>Phytolacca acinosa</i>	Phytolaccaceae	1.9%	Field survey and hydroponics experiment; Hoagland's nutrient solution was applied; plants were exposed to 0–15,000 μmol Mn L <sup>-1</sup> (as MnCl <sub>2</sub> ·4H <sub>2</sub> O); Hunan Province, China	Xue et al. [115]
<i>Polygonum pubescens</i>	Polygonaceae	1.6%	Field survey and hydroponics experiment; Hoagland solution applied; Plants exposed to 0–20 mmol Mn L <sup>-1</sup> (as MnCl <sub>2</sub> ·4H <sub>2</sub> O); China	Deng et al. [116]
<i>Polygonum lapathifolium</i>	Araliaceae	1.4%	Field survey and hydroponics experiment; Hoagland solution was applied; plants exposed to 0–16 mmol Mn L <sup>-1</sup> (as MnCl <sub>2</sub> ·4H <sub>2</sub> O); Guangxi Province, China	Liu et al. [117]
<i>Schima superba</i>	Typhaceae	1.2%	Pot experiment; Hoagland solution was added as a fertilizer; <i>S. superba</i> saplings were exposed to 0–200 mmol L <sup>-1</sup> MnCl <sub>2</sub> ·4H <sub>2</sub> O; China	Yang et al. [118]
<i>Viotia neurophylla</i>	Typhaceae	5.5%	Ex situ; plant analysis; Semi-tropical climate; New Caledonia	Jaffré [108]

### 2.1.6. Selenium

Selenium (Se) levels in soil are often lower than 2 mg kg<sup>-1</sup>, but they can increase to a few hundreds of mg kg<sup>-1</sup>. The selenium concentration in plants dry biomass is typically lower than 0.1 mg kg<sup>-1</sup> and may even be as low as 0.01 mg kg<sup>-1</sup>. Nonetheless, it was discovered that legumes belonging to the *Astragalus* genus were able to accumulate Se to elevated concentrations, locally exceeding 1000 mg kg<sup>-1</sup> in the USA in Se-rich soils [119]. Table 7 shows the 20 hyperaccumulators for Se. Due to the typically low levels of Se in plant tissues, Reeves [20] argued that a limit of 100 mg kg<sup>-1</sup> should be considered for identifying Se hyperaccumulators. To date, utilizing Se hyperaccumulators for the economic extraction of Se has not been suggested. However, there are potential uses of these plant species in phytoremediation for cleaning up contaminated soils in crops harvested for stock feed and Se biofortification [120].

### 2.1.7. Thallium

Thallium is a precious metal high in demand but comparatively rare in nature. Although it is very toxic and difficult to find in the environment, natural, along with anthropogenic, origins can introduce significant amounts of Tl in soil. Several plant species are capable of extracting Tl from soils, making them useful for reclaiming it. Specifically, according to Leblanc et al. [130], there was an unexpected accumulation of Tl in *Iberis intermedia* and *Biscutella laevigata* in Pb/Zn mines in France. Moreover, for *I. intermedia*, an uptake of 4000 mg of Tl kg<sup>-1</sup> was reported and over 14,000 mg kg<sup>-1</sup> DW for *B. laevigata*, where the background concentration of Tl was 10 mg kg<sup>-1</sup> in mine tailings. The presence of Tl in soil at levels that make Tl PM feasible is a possibility. However, there are only a

few sites where this could be realistically implemented due to the limited availability of suitable soil conditions.

**Table 7.** List of Se hyperaccumulator species.

Plant Species	Family	Achieved Concentration (mg kg <sup>-1</sup> )/Biomass Yield (t ha <sup>-1</sup> )	Experimental Conditions—Country	Reference
<i>Asparagus bisculatus</i>	Asparagaceae	0.88%/12.3	Ex situ; plant analysis; Canada	Reeves [121] Moon [122]
<i>Asparagus patersonii</i>	Asparagaceae	0.25%/12.3	Ex situ; plant analysis; USA	Reeves [121] Moon [122]
<i>Asparagus pectinatus</i>	Asparagaceae	0.51%	Ex situ; plant analysis; USA	Reeves [121]
<i>Asparagus racemosus</i>	Asparagaceae	1.5%	Ex situ; plant analysis; USA	Reeves [121]
<i>Atriplex canescens</i>	Amaranthaceae	0.17%/34.75	Ex situ; plant and soil analysis; Arid climate; Algeria	Nadaf et al. [123]; Nedjimi [124]
<i>Castilleja chromosa</i>	Orobanchaceae	0.18%	Ex situ; plant analysis; USA	Reeves [121];
<i>Cardamine violifolia</i>	Brassicaceae	0.48%	Ex situ; plant analysis; Korea and Yutangba, China	Ma et al. [125] Huang et al. [126]
<i>Lecythis ollaria</i>	Lecythidaceae	1.8%	Ex situ leaf analysis; Venezuela	Reeves [121]
<i>Machaeranthera gabriulscula</i>	Asteraceae	0.18%	Ex situ leaf analysis; USA	Reeves [121]
<i>Machaeranthera parryi</i>	Asteraceae	0.53%	Ex situ; leaf analysis; USA	Reeves [121]
<i>Machaeranthera ramosa</i>	Asteraceae	0.13%	Ex situ; leaf analysis; USA	Reeves [121]
<i>Machaeranthera venusta</i>	Asteraceae	0.34%	Ex situ; leaf analysis; Colorado, USA	Reeves [121]
<i>Neptunia amplexicaulis</i>	Fabaceae	0.11%/43.3	Pot experiment; soil spiked with 0, 5, and 30 mg Se kg <sup>-1</sup> (as Na <sub>2</sub> SeO <sub>4</sub> or CaSeO <sub>3</sub> ); Queensland, Australia	O'Donohue et al. [127]; Irish et al. [128]
<i>Stanleya bipinnata</i>	Brassicaceae	0.23%	Ex situ; leaf analysis; USA	Reeves [121]
<i>Stanleya pinnata</i>	Brassicaceae	0.11%	Climate controlled experiment; Hoagland solution applied as fertilizer; plants exposed to 0–80 μM N <sub>2</sub> SeO <sub>4</sub> ; Colorado, USA	Harris et al. [129]

### 2.1.8. Noble Metals

Recently, NMs are being examined for their PM potential. This category constitutes metals such as gold (Au) and silver (Ag), as well as a sub-group of platinum metals including iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh), and ruthenium (Ru) [15]. These metals find extensive use across different industries and are often referred to as precious metals, obtaining significant attention due to their economic value. Interestingly, while the demand for NMs increases, their primary ore sources are gradually depleted. Hence, alternative methods of extraction, like PM, are being explored. Recent research and development on the extraction and accumulation of these metals in plants has shed light on the PM pathway for recovering these metals, although real-time implementation remains limited [131]. It should be noted that NMs can not be absorbed by plants from the metallic state as plants are capable of absorbing only the soluble species of any inorganic element found in the soil solution.

## Gold

Across the world, considerable quantities of Au deposits can be found in natural enriched soils and mine tailings. Mohan [132] mentioned that PM of Au is a cost-effective way to extract Au from mine tailings and low-grade ores. Conventional mining removes the most Au from ores, leaving behind a significant portion of Au that cannot be extracted due to economic disadvantages. Since 1988, the hyperaccumulation limit of Au has been set to be higher than  $1 \text{ mg kg}^{-1}$  DW, based on the normal concentrations of Au in plants, which are usually around  $0.01 \text{ mg kg}^{-1}$ . However, Au must be in the soluble form before absorption can take place. This can be achieved by adding several types of lixiviants (e.g., NaCN,  $\text{SCN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ) depending on the properties of the substrate. In low-pH sulphate containing substrates, thiocyanate can solubilize Au.

It is reported that conifers growing in areas with Au ores in Canada could accumulate up to  $0.02 \text{ mg}$  of Au  $\text{kg}^{-1}$ , while the background levels in plants are 100 times lower [133]. Also, in an experiment where *Brassica juncea* was planted in pots containing  $5 \text{ mg Au kg}^{-1}$  in artificial substrate, Anderson et al. [134] concluded that the application of  $160 \text{ mg}$  of ammonium thiocyanate  $\text{kg}^{-1}$  of dry substrate weight achieved an accumulation of  $57 \text{ mg Au kg}^{-1}$ . Wilson et al. [135] also referred to research where *B. juncea* was able to absorb  $63 \text{ mg Au kg}^{-1}$  DW after soil was treated with sodium cyanide. The plants were grown on an oxidized ore pile containing  $0.6 \text{ mg Au kg}^{-1}$ . They concluded that an economically viable option for Au extraction that could yield  $1 \text{ kg}$  of Au  $\text{ha}^{-1}$  would require a total harvested biomass of  $10,000 \text{ kg ha}^{-1}$  containing  $100 \text{ mg kg}^{-1}$ . Furthermore, Msuya et al. [136] mentioned that carrots (*Daucus carota*) accumulated  $0.779 \text{ mg ha}^{-1}$  of Au when ammonium thiocyanate was added and  $1.45 \text{ mg ha}^{-1}$  when thiosulphate was added, while the concentration of Au in the growing substance was  $3.8 \text{ mg kg}^{-1}$ . Lamb et al. [137] performed a study where they used cyanide and thiocyanate to test the accumulation of Au in *Berkheya coddii*, *Brassica juncea*, and *Cichorium intybus*. They found that the leaves of *B. juncea* and *C. intybus* in soils spiked with cyanide had the highest Au accumulation at a rate of  $326 \text{ mg kg}^{-1}$  (*B. juncea*) and  $164 \text{ mg kg}^{-1}$  (*C. intybus*). Another study conducted by Vural and Safari [138] evaluated the potential of *Helichrysum arenarium* for Au accumulation; they reported TF and BAF values of 2.04 and 0.59, respectively. They concluded that enhancing the availability of Au in soil by adding chelators like NaCN,  $\text{SCN}^-$ , and thiosulfates can lead to the usage of *Helichrysum arenarium* in the PM process.

## Silver

To date, there are no reports about the hyperaccumulation of Ag by plants. Even though the Ag concentration in plants can be up to  $1 \text{ mg kg}^{-1}$ , some plants such as *Lupinus angustifolius* can reach up to  $126 \text{ mg kg}^{-1}$  by induced accumulation [5]. Harris and Bali [139] were the first to propose the uptake of Ag nanoparticles by plants. They conducted research in which they observed an accumulation of significant amounts of Ag in *Brassica juncea* and *Medicago sativa* plants. Specifically, *B. juncea* absorbed up to 12.4% of its weight in Ag when exposed to  $1000 \text{ mg L}^{-1}$  of  $\text{AgNO}_3$  for 72 h, while *M. sativa* accumulated up to 13.6% of its weight in Ag when exposed to a solution containing  $10,000 \text{ mg L}^{-1}$   $\text{AgNO}_3$  for 24 h. Silver nanoparticles that were stored inside the plant's tissues had a size of 50 nm. In addition, the application of EDTA was not helpful in enhancing the absorption of Ag. EDTA had a rather negative effect as it caused toxicity to plants and this decreased the amount of Ag that would otherwise be capable for extraction. They concluded that plants could be used to produce large quantities of metallic nanoparticles.

## Palladium

Out of all the platinum group metals, Pd has gathered significant attention due to its high abundance compared to others. The first report for Pd accumulation in plants was made by Fuchs and Rose [140], who measured a concentration of  $285 \text{ } \mu\text{g kg}^{-1}$  in ash from *Pinus flexilis*. In addition, Kothny [141] reported an accumulation of  $400 \text{ } \mu\text{g kg}^{-1}$  of Pd in the ash of *Quercus chrysolepsis*, while the background level was  $140 \text{ } \mu\text{g kg}^{-1}$ . The hyperaccumulator

*Berkeya coddii* was investigated for its ability to absorb Pd by Nemutandani et al. [142] from a contaminated site with  $70 \mu\text{g kg}^{-1}$  Pd. It was found that *B. coddii* was able to extract  $180 \mu\text{g kg}^{-1}$  in roots and  $710 \mu\text{g kg}^{-1}$  in leaves. The plant demonstrated a notable ability to accumulate and translocate Pd, with BAF and TF values reaching 10.1 and 3.9, respectively.

There have been no officially defined Pd hyperaccumulators; it is anticipated that the threshold for all NMs would be approximately  $1 \text{ mg kg}^{-1}$ , assuming their normal low concentration in plants. On the other hand, Pd, like Au, has limited solubility in soil. Hence, soil amendments are often used in order to increase Pd solubility and improve the accumulation in plants. For instance, KCN has been utilized to increase the absorption of Pd by plants. Walton [143] used KCN at a rate of  $10 \text{ g L}^{-1}$  to enhance Pd accumulation in *B. coddii* when cultivated in mine tailings containing  $315 \mu\text{g kg}^{-1}$ . They reported that plants had accumulated Pd to levels as high as  $7677 \mu\text{g Pd kg}^{-1}$ . In addition, Aquan [144] conducted an experiment utilizing gossan rock as a substrate, containing  $205.5 \mu\text{g Pd kg}^{-1}$ . They assessed the Pd accumulation in *Cannabis sativa* and found that the average Pd concentration was  $30,336 \mu\text{g kg}^{-1}$  in the aboveground part of the plant, reaching as high as  $62,420 \mu\text{g kg}^{-1}$  when KCN was applied. Another study conducted by Harumain et al. [145] managed to trigger the hyperaccumulation of Pd in *Salix purpurea* and *Miscanthus* through the use of KCN. They employed a synthetic ore with a Pd concentration of  $50\text{--}100 \text{ mg kg}^{-1}$  as growth medium. As a result, the leaves of *S. purpurea* and *Miscanthus* were found to contain  $820$  and  $505 \text{ mg kg}^{-1}$ , respectively. Overall, the idea of phytomining Pd is relatively new. The effectiveness of using plants to extract this valuable element has only been minimally demonstrated so far.

### Platinum

While the potential of plants to accumulate Pt in its tissues was mentioned by Fuchs and Rose [140], it is noteworthy that numerous studies on Pt PM have emerged recently. Nemutandani et al. [142] revealed that *B. coddii* grown in Pt-polluted areas with concentrations of  $0.04 \text{ mg kg}^{-1}$  soil achieved an uptake of  $0.22 \text{ mg kg}^{-1}$  in leaves and  $0.18 \text{ mg kg}^{-1}$  in roots. The plant exhibited BAF (5.5) and TF (1.2) values greater than 1.0, highlighting its ability to accumulate and translocate Pt. A study conducted by Kovacs et al. [146] reported the identification of plants from contaminated brownfield land with a Pt concentration of  $3.06 \text{ mg kg}^{-1}$ . Also, Diehl and Gagnon [147] found concentrations of  $14.6 \text{ mg kg}^{-1}$  in *Daucus carota* collected from an area near a heavy-traffic motorway. White mustard, *Sinapis alba*, was also reported to show great ability in accumulating Pt by Kińska and Kowalska [148]. They found an impressive accumulation of  $5973 \text{ mg kg}^{-1}$  dry root weight, while the concentration of Pt in the nutrient solution was  $1.0 \text{ mg L}^{-1}$ . Despite numerous reports on Pt in plants, it is worth mentioning that experiments aimed at Pt PM have not been conducted.

### Rhodium

Generally, studies regarding the occurrence of Rh in plant tissues are very limited due to its scarce presence. A study conducted by Diehl and Gagnon [147] reported a Rh concentration of  $0.7 \text{ mg kg}^{-1}$  in *Daucus carota* that was collected from four different areas near heavy-traffic roads. Bonanno [149] found that the Rh concentration in *Phragmites australis*, collected from an extremely urbanized riverside area, ranged from  $1.11$  to  $1.13 \text{ mg kg}^{-1}$ . Generally, it is worth noting that Rh has the highest solubility among the platinum group elements [15]. This suggests that Rh has great potential use in PM applications.

## 2.2. Factors Influencing Metal Availability and Behavior in Soil

### 2.2.1. pH

Soil activity plays a crucial role in how easily certain nutrients can dissolve in the soil solution and be taken up by the plants. As a result, soil pH affects the ability of plants to absorb essential nutrients and other elements from soil. For instance, Punjari [150] reported that when the pH of soil drops below 6.5 and 5.3, the amount of soluble Cd and Zn increases.

Likewise, the solubility of Cu and Pb increases at pH levels below 4.5 and 3.5, respectively. On the other hand, at this low pH level, the mobility of As ions decreases. This is related to the fact that As is present in the soil solution as oxyanion, either in its trivalent (arsenite;  $\text{As}^{\text{III}}\text{O}_3^{3-}$ ) or its pentavalent species (arsenate;  $\text{As}^{\text{V}}\text{O}_4^{3-}$ ). The same is the case with any other contaminant anions (such as hexavalent chromium;  $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ )—their availability is proportional to soil pH. The significance of pH in determining metal solubility and availability can be indicated by the fact that the pH in the root zone of certain plants is often up to 2 units lower than the surrounding soil pH due to the release of organic acids [151]. The amount of metal extraction is directly related to the concentration of the metal in soil and pH of the extracting agent.

There are various ways to reduce soil pH. This can be achieved by using different substances, including fertilizers containing ammonia, acids, and zero-valent sulfur, as amendments. However, there are limitations as to how much the pH can be lowered because most plant species can only thrive within a specific pH range. Usually, the lowest pH that many plants can tolerate is c. 4.5 [5]. Hence, while it is possible to adjust the pH utilizing soil amendments, it is important to carefully consider the range that allows plants to grow without adverse effects. On the other hand, acidic pH values can be corrected with the application of “liming” materials, which are mainly phases with abundant inorganic carbonate phases, i.e.,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ , such as marble dust (either calcitic or dolomitic), as well as their derivative, caustic calcium oxide. Robinson et al. [45] studied the effects of different substances, namely  $\text{MgCO}_3$ ,  $\text{CaCO}_3$  (both alkalinity-bearing materials), and sulfur (an acidifying material), on the uptake of Ni and Co by *Berkeya coddii*. When  $\text{MgCO}_3$  was added to the soil, it increased the soil pH from 6.9 to 8.7 which led to reduced uptake of Ni and Co by *B. coddii*. On the other hand, the application of sulfur resulted in a decrease in soil pH from 6.9 to 5.5, which increased the plant’s uptake of both metals. In addition, the application of Ca salts made plants tolerant to Ni [8]. The authors concluded that the addition of acidifying materials, like sulfur, can help extract more metals from soil by making them more available to plants. The shoot Ni concentration increased in *Alyssum* sp. at pH levels ranging from 5 to 7, with maximum concentrations being obtained at a pH of 6.5 [152]. The same relationship between cationic metal species and soil pH (which is inversely proportional—the former increases when the latter decreases and vice versa) has repeatedly been confirmed in experimental studies [36,110]. This was also found by Zhong et al. [153] in soil samples collected from heavy metal-contaminated soils in China; they reported a significant availability in soil for Ni, Zn, Cu, Cd, and Cr at pH levels lower than 4.5. They also concluded that soil pH is the most important factor concerning metal availability in soil. Specifically, pH was reported to affect all physicochemical and biological processes in soil, which in turn affect the behavior and the way metals interact with other substances. Since acidic pH tends to decrease metal sorption in soil, metal availability increases due to increased metal concentration in soil solution.

### 2.2.2. Fertilizers

In order to successfully implement the technique of PM, the availability of metals in soil needs to be ensured. Besides optimizing soil pH levels to guarantee metal absorption, adding fertilizers to achieve high-yielding phytoextraction crops is another factor that needs to be mentioned. Fertilizers containing  $\text{NH}_4\text{-N}$  can reduce soil pH due to the fact that  $\text{NH}_4^+$  in aerated soils is readily oxidized within weeks to  $\text{NO}_3^-$ , a process yielding 2 mols of  $\text{H}^+$  per mol of nitrified N. This enhances further the availability of metals in soil, as well as providing optimal conditions for the growth of these certain plant species [154]. In fact, hyperaccumulators grown in soils derived from ultramafic rocks exhibit a noticeable positive response to the application of fertilizers. For instance, in Vertisols in Albania, there was a 10-fold increase in the yield of *A. murale* after applying inorganic fertilizers [23].

Sheoran et al. [5] highlighted that the application of fertilizers significantly increased the maximum annual growth of *Alyssum bertolonii* compared to the non-fertilized treatment, which resulted in higher biomass yields. Specifically, the application of NPK fertilizers

achieved an overall increase of 308%. Thus, fertilization can greatly affect the phytoextraction process, to remove metals from soil, making it more effective. The same work reported that Ni levels were increased in the leaves of *Berkeya coddii* from 2500 mg kg<sup>-1</sup> to 4200 mg kg<sup>-1</sup>. Similar results were reported by Bennett et al. [155], where the application of NPK fertilizers doubled the annual biomass production of *Alyssum bertolonii*, *Streptanthus polygalonoides*, and *Thlaspi caerulescens*, without reducing the concentration of Ni in their shoots. In another study, the application of 100 kg P ha<sup>-1</sup> in serpentine soils led to an improved yield in *Alyssum murale* plants [7]. Overall, high N fertilization promotes higher accumulation of Ni, Cd, and Zn. Sheoran et al. [156] used *Salix* on contaminated soil containing low levels of Cd (1.9–2.4 mg kg<sup>-1</sup>) and showed that the application of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at 100 mg N kg<sup>-1</sup> significantly increased the Cd and Zn plant concentrations to 4.5 for Cd and 400 mg kg<sup>-1</sup> for Zn. Similar results were reported by Schmidt [157], who noticed a significant increase in Cd in *Lolium perenne* after adding (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as fertilizer. In that same work, in soils with low concentrations of Zn and Ni, the application of this fertilizer also significantly increased the crop metal concentrations without any loss of total yield. The same was agreed by Babau et al. [158], who tested *Robinia pseudoacacia* for its ability to absorb Pb, Cd, and Cu with and without the presence of NPK fertilizer. We conclude based on the above-reviewed literature that the addition of nutrients to soil (mostly N) increases the ability of plants to absorb metals and thus it is likely to increase the phytomining effectiveness of hyperaccumulators; hence, fertilizers are considered a critical factor for the success of commercial PM processes.

### 2.2.3. Chelates

In hyperaccumulators, the number of metals these plants can remove from soil depends on biomass production and the concentration of the metals within their tissues; thus, often their extraction ability is limited [159]. In order to increase the extraction of metals, chelates can be a possible option for higher growth rates. Chelates are capable of extracting various metals from soil. They have the ability to bind metals and form water-soluble organometallic complexes. Once they are formed, they can introduce metals into the soil solution by removing them from the surfaces they were attached to [160]. Some of the most used chelating agents are EDTA (ethylenediaminetetraacetic acid), CA (citric acid), DTPA (diethylenetriaminepentaacetic acid), NTA (nitroloenetriacetic acid), EDDS (ethylenediaminedisuccinic acid), and thiosolutions like thiocyanates. The former two agents are the most widely utilized [10,161]. Specifically, Robinson et al. [162] used EDTA and CA on *B. coddii* in order to phytomine Ni. Interestingly, they found that even though soluble Ni increased in the rhizosphere, the Ni concentration in the shoots decreased. They concluded that competition between EDTA, CA, and the plant's own excreted resulted in trapping Ni in the root system of the plant. However, Meers et al. [163] reported an increase in Ni uptake in sunflowers which was 1.8 to 2.8 times greater by adding 1.6 mmol kg<sup>-1</sup> EDTA and EDDS. Another study conducted by Blaylock et al. [164] where EDTA was applied in heavy metal-contaminated soils showed an enhanced accumulation of Pb, Cd, Cu, and Zn in *Brassica juncea* shoots. Nevertheless, they concluded that chelators like EDTA may pose an environmental risk due to the fact that they can not be easily degradable by soil microbes, resulting in groundwater pollution. Additionally, Wang et al. [165] reported results from a field experiment where soil-applied EDTA and EDTA–ethyl lactate were found to enhance Cd extraction by 20 and 29%, respectively, in *Salix*. Gold has also been found to accumulate in plants like *Brassica juncea*, *Zea mays*, *Daucus carota*, and *Cichorium* spp. by adding chelate agents like thiosolutions.

## 3. Metal Accumulation in Plants and Their Subsequent Recovery

### 3.1. Mechanisms of Metal Accumulation in Plants

The process of metal hyperaccumulation in plants, and thus phytomining, consists of several different stages that plants go through. Making the soil in the immediate vicinity of the plant's roots more acidic and releasing organic compounds is one of the

plant's strategies to absorb metals from soil. The acidification of soil can occur due to the secretion of hydrogen ions ( $H^+$ ), which can help in dissolving metals and making them available for absorption. This process is carried out by essential enzymes like the  $H^+$  pumps, such as the plasma-membrane  $H^+$  ATPases [164]. Additionally, roots excrete organic acids, such as malonic and oxalic, as well as enzymes and metal-chelating molecules, like phytosiderophores. These substances have the ability to enhance the absorption of metals from soil by binding them and thus assist their phytomining [166]. The movement of metals inside the plant cells can have two potential pathways, which are the apoplastic flow and the symplast transport. Metals can enter the root apoplast, which is the space between cells in the root. Even though solutes are capable of moving upwards through the plant using this pathway, the more effective way is through the plant's vascular system, the xylem [5]. Moreover, to enter the xylem, where long-distance transport occurs, metals have to go through the Casparian strip, which is a waxy layer of cells that surrounds the xylem and is impermeable to solutes. Thus, metals must cross membranes aided by pumps or channels in the endodermal cells. After crossing the Casparian strip or membranes, the movement of metals within the xylem is called "symplast transport". Symplast transport is more regulated than apoplastic flow because the movement of metals is controlled by the properties of the cell membranes and the presence of specialized transport proteins or channels that facilitate their movement [164]. Generally, plants have the ability to manage heavy metals, avoid toxicity, and store them safely [167]. Different oxidation levels of heavy metals have varying characteristics during absorption, conveyance, and detoxing within the plant. After being translocated to shoot cells, metals can be stored in specific cellular locations such as in the apoplast, epidermis cells, the mesophyll, and cell walls, where they will not disrupt any cellular processes. This is achieved by sequestering metals away from cellular processes that could otherwise be harmed. The trapping of the metals often takes place in plant vacuoles [168].

### 3.2. Metal Recovery

To recover the metals accumulated in plants, various metal extraction technologies are employed. However, before extraction can be undertaken, the plant biomass needs to be reduced to a manageable quantity so that any plant-borne metals may be concentrated in the remaining material. This is crucial for reduction in the transportation costs, as well as the size of machinery used for metal extraction. Biomass reduction can occur in various ways, including composting, compaction, and thermal conversion.

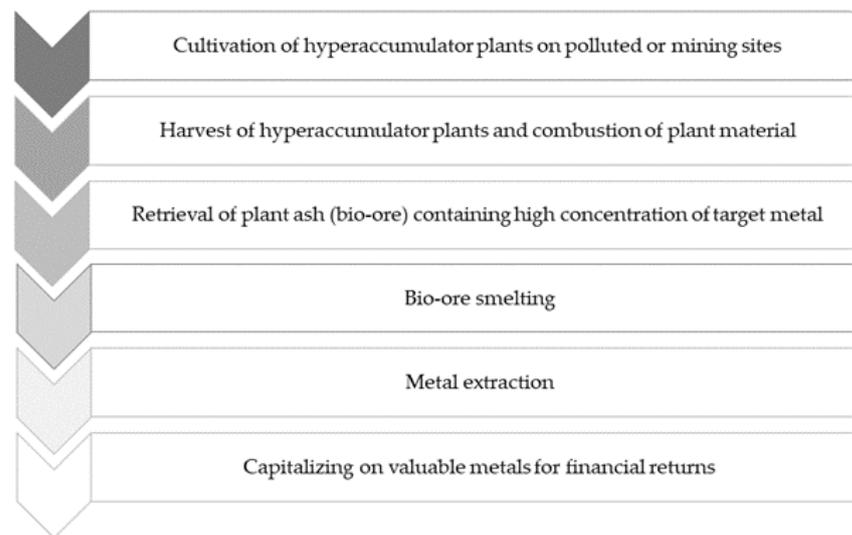
According to Hu and Gholizadeh [169], the thermal conversion methods of combustion and ashing are considered to be the most practical for concentrating metals. In fact, these processes involve high temperatures, ranging from 350 to 1000 °C, that lead to fast reaction times and effective biomass volume reduction. During combustion, the polluted biomass turns into gas and energy is released as heat. Metals cannot easily escape as gases during the process, resulting in the formation of ash containing high concentrations of valuable metals. On the other hand, unwanted emissions of C and N oxides are issues that need to be considered. However, the overall approach is considered to be a neutral C-releasing activity in terms of greenhouse gas emissions due to the fact that C can be captured and be stored via oxy-fuel combustion [15].

Ashing is the same process as combustion but takes place at lower temperatures (300–550 °C) and is commonly used in laboratory environments for analytical purposes. For instance, Zhang et al. [170] found that the best conditions of biomass combustion for Ni recovery were ashing at 550 °C for a duration of 3 h. By doing this, they were able to obtain high quality ash reaching 20% of the weight of Ni. However, according to Dastyar et al. [171], in order to recover good quality ash, it is important to understand the behavior of metal dynamics during thermal conversion. Specifically, metal behavior is influenced by various factors, including the type of plant biomass, the equipment that is being used, and combustion conditions like temperature, pressure, and duration. For example, Hazotte et al. [172] compared metal concentrations in three Ni hyperaccumulators

(*Odontarrhena chalcidica*, *Leptoplax emarginata*, and *Berkheya coddii*), along with biomass volume reduction in two different temperatures (550 and 900 °C) and standard pressure. They reported that the Ni concentration at 900 °C was higher compared to that at 550 °C in all three hyperaccumulator plant tissues. In addition, they reported that at 550 °C, over 95% of the organic material was broken down and 99% of C was eliminated from all plant species. They concluded that combustion is an effective method for the degradation of plant biomass, while achieving high concentrations of metals with no notable loss up to 900 °C. In another study conducted by Kovacs et al. [147], Au could not be detected in the woody biomass. Nevertheless, after the combustion of plant material, Au could be detected in the residual solid, where it exhibited a considerable concentration of 4.10 mg kg<sup>-1</sup>. Nevertheless, despite findings regarding the importance of biomass combustion and ashing, there is rather limited information in the literature regarding enrichment in the solid residues with valuable phytomined metals.

After biomass combustion or ashing are finished, a metal-rich ash is obtained. However, it may still contain impurities that need to be further processed in order to isolate the target metal. This can be achieved by employing pyrometallurgical, hydrometallurgical, and bio-metallurgical methods. Pyrometallurgy refers mainly to the traditional process of smelting, but it can contain other methods too, such as incineration, chlorination, and volatilization [15]. Pyrometallurgy involves the use of high temperatures to separate the metals from other materials. However, the environmental effects of this method, like the release toxic fumes, and the expensive equipment, are some limitations of this approach. Hydrometallurgy involves the use of leaching agents in order to extract and separate the metals. Metals within the solution are separated and isolated by utilizing various techniques, including ion capture, liquid separation, ion exchange, and electrochemical reduction. Compared to pyrometallurgy, hydrometallurgy is easier to use, offers great metal selection, is efficient in recovering metals, and less expensive in terms of equipment. Interestingly, most of the studies examine the use of both methods for isolating metals. For instance, Lamb et al. [137] managed to isolate Au from woody plant material after ashing the biomass and using 2 M HCl as a leaching agent. The solution was separated by adding methyl isobutyl ketone, followed by the addition of sodium borohydride. This resulted in the formation of a black deposit which was heated at 800 °C, which led to the formation of pure Au.

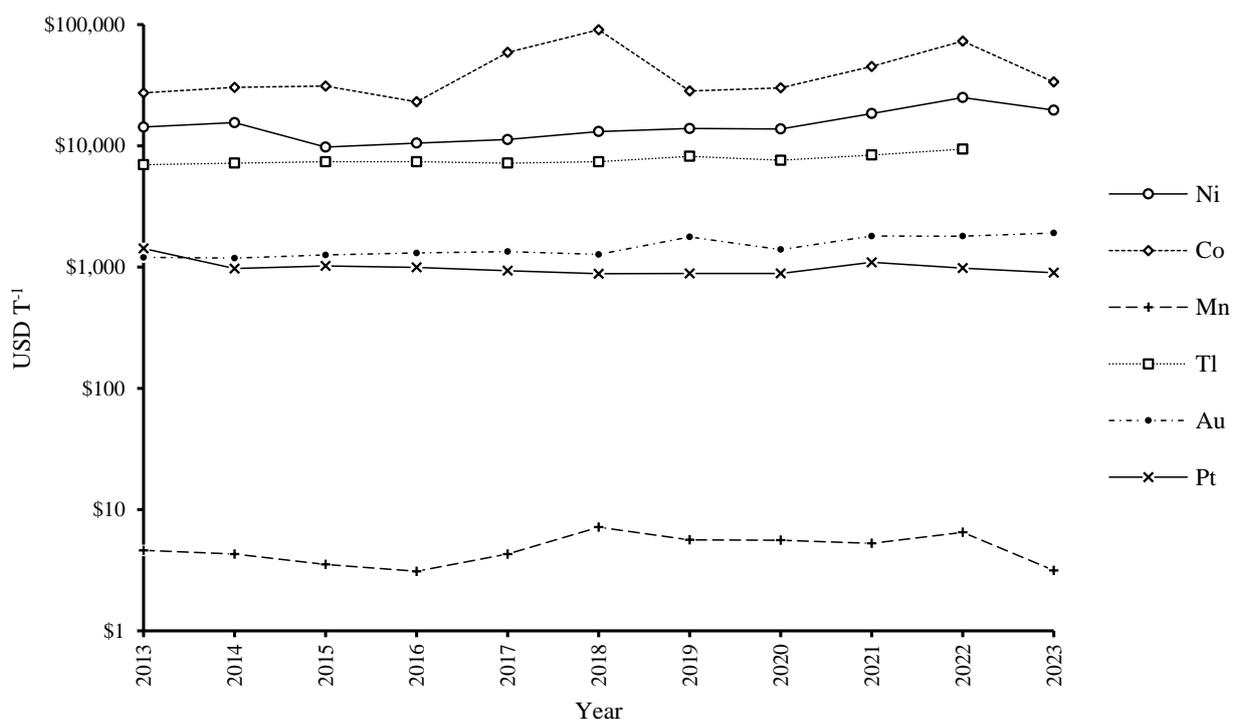
During the last decade, a new approach called bio-metallurgy has become popular for recovering metals. It consists of two main parts: “bioleaching” and “biosorption”. Bioleaching refers to the use of microorganisms, like bacteria, fungi, and algae, to interact with metals through oxidation-reduction reactions. Bioleaching has been considered to be an eco-friendly and economically viable option. However, it is not efficient enough for metal recovery and it takes a lot of time to be completed, which leads to restricted use and means it is only used for laboratory-scale operations [173]. On the other hand, biosorption utilizes microbes, fungi, yeasts, algae, and waste products, which are used to collect metals. These organisms act like “magnets” by entrapping metals through physical and chemical interactions between metals and the surface of these microbes. Generally, biosorption has emerged as a cost-effective and environmentally friendly technique compared to traditional methods, especially for aquatic media [174]. Processes are shown in Figure 1.



**Figure 1.** Main stages in the phytomining process for metal extraction.

#### 4. Financial Considerations of Phytomining

The economic success of PM relies on several factors, such as (i) the metal content in soil and plants, (ii) the amount of biomass production, and (iii) the amount of retrieved (or phytomined) metal that can be recovered during the combustion of the produced biomass which can then be captured and sold. However, the most imperative factor for PM is the revenue generation, which depends on the market demands and the world price of the metal being extracted through plants [10,174]. Metal prices can vary from USD  $0.75 \text{ kg}^{-1}$  for Fe ores to USD  $61,375 \text{ kg}^{-1}$  for Au [175]. As a result, metals with high prices offer better economic prospects. Precious metals can be very costly and their price keeps rising consistently (Figure 2); thus, there must be a sufficient amount of these metals in the harvested biomass in order for the PM process to be profitable. The economic proposed concentration of precious metals is shown in Table 8.



**Figure 2.** Metal price trends of the last decade.

**Table 8.** Economically viable concentrations of precious metals in the harvested biomass that are necessary to make the phytomining process profitable.

Element	Natural Occurrence in the Earth's Crust (mg kg <sup>-1</sup> )	Economically Viable Plant Metal Concentration (mg kg <sup>-1</sup> )	Economic Proposed Concentration in Biomass (mg kg <sup>-1</sup> )	Reference
Au	0.0040	6	0.06–0.6	Lee et al. [176]
Ag	0.0750	1000	10–100	Lee et al. [176]
Pd	0.0150	5–15	0.05–1.5	Lee et al. [176]
Pt	0.0050	4	0.04–0.4	Dinh et al. [15]
Rh	0.0010	5–15	0.05–1.5	Dinh et al. [15]

Manganese is an example of an element where even though its price is low, USD 6.5 t<sup>-1</sup>, there are certain plants that can accumulate large quantities of it. Macadamia plants have been reported to accumulate high concentrations of Mn in their tissues; therefore, they can be a feasible and profitable option. However, metal prices often undergo cycles of fluctuations—PM may be viable, if technically possible, even while current market prices happen to be low. There is always the capability of combusting the biomass which contains the extracted metal to recover the economic value; metals can be extracted from plants and the remaining material can be burned to generate energy. After combustion, the ash could be stored until the world price of the extracted metals improves [10,174]. Moreover, companies do not only make profit just from the PM process but also from harnessing the biomass for energy production. Additionally, they may be utilizing the resulting ash as a source of C and potash. Furthermore, they may be deriving advantages from the sale of CO<sub>2</sub> credits [57].

As mentioned earlier, during the first field experiment for extracting Ni, *Streptanthus polygaloides* yielded a total dry biomass of 10,000 kg ha<sup>-1</sup> containing 10,000 mg kg<sup>-1</sup> Ni. It is reported that a net profit of USD 513 ha<sup>-1</sup> could be achieved with a price of USD 7.65 kg<sup>-1</sup> at that time. In addition, a net return of USD 131 ha<sup>-1</sup> could be achieved due to energy yield during the combustion of the biomass, leading to a gross return of USD 765 ha<sup>-1</sup>. Considering Ni current prices, of approximately USD 20 kg<sup>-1</sup>, such yields and Ni uptake could achieve a gross profit of USD 1341 ha<sup>-1</sup>. Anderson et al. [177] utilized the Tl hyperaccumulator *I. intermedia* and extracted 8 kg ha<sup>-1</sup> of Tl in a total of 10,000 kg ha<sup>-1</sup> dry biomass, which was worth a total of USD 2400. This means that a crop with 10,000 kg ha<sup>-1</sup> of biomass would need to accumulate at least 170 mg kg<sup>-1</sup> Tl, which is achievable by *I. intermedia*. On the other hand, as previously stated, *B. laevigata* produces lower biomass (4000 kg ha<sup>-1</sup>), which means that an average of 425 mg Tl kg<sup>-1</sup> is required—it was found that 39% of the plants surpassed this threshold in that work. Selling biomass for power generation could also add a profitable amount to the farmer's income.

In addition, Nkrumah et al. [178] suggested the use of both an intensive and extensive Ni production system. Moreover, both approaches were found to be profitable. Extensive systems are those where the only costs are herbicides, fertilizers, and any management practices, while an intensive production system requires additional labor and equipment costs. They even made a hypothetical scenario where they calculated the economic potential of Ni PM, comparing the two approaches. Specifically, they (a) considered an average market price of USD 18 over a 5-year period from 2010 to 2015, (b) estimated the amount of Ni that plants can produce in the two systems, which was leveled at 200 kg ha<sup>-1</sup> for the intensive system and 110 kg ha<sup>-1</sup> for the extensive, (c) calculated the cost of the production in 2016, which was approximately USD 1074 ha<sup>-1</sup> year<sup>-1</sup> and USD 600 ha<sup>-1</sup> year<sup>-1</sup> for the intensive and the extensive systems, respectively, and (d) included in that about 20% of the value of Ni that would cover expenses and costs associated with metal recovery from plants. Assuming these factors, they calculated the gross values of an annual PM crop, which was found to be USD 3600 ha<sup>-1</sup> year<sup>-1</sup> for the intensive system and USD 1980 ha<sup>-1</sup> year<sup>-1</sup>

for the extensive system. After accounting the costs that were mentioned before, they measured a net value of USD 1806 ha<sup>-1</sup> year<sup>-1</sup> for the intensive system and a net value of USD 980 ha<sup>-1</sup> year<sup>-1</sup> for the extensive system. In addition, other sources for enhancing profit could be harnessing energy from combustion or selling carbon credits for reducing gas emissions.

Lee et al. [176] mentioned the remarkable metal-accumulating abilities of *Haumanias-trum robertii* and *Aeolanthus biformifolius*. Specifically, *H. robertii* is capable of accumulating up to 1% of its dry biomass as Co, while *A. biformifolius* can accumulate up to 1% of its dry biomass as Cu. As a result, commercial use of *H. robertii* can lead to a harvest of 200 kg Co per 20 t of dry biomass per year. Assuming 100% Co recovery and a current Co market price per ton of USD 33,618, this could potentially result in USD 6723 of income ha<sup>-1</sup> per year. Similarly, *A. biformifolius* has the potential to yield 200 kg of Cu from 20 t of dry biomass ha<sup>-1</sup> per year. Assuming 100% Cu recovery and a current market price of USD 7963 for Cu, this could lead to a gross income of USD 1592 ha<sup>-1</sup> per year.

As the process of PM continues over time, the ore deposits eventually get depleted, making it less economically viable to obtain them. Nevertheless, compared to the conventional mining methods, the time when it will no longer be cost effective to mine these metals through PM is much higher. This is because PM is a cost–benefit method. Moreover, plants used in the PM process can have a multifaceted application until the soil where they are planted is ready for food production once again. Ongoing research towards a better understanding of the mechanisms involved in the PM process, along with other improvements, is expected to extend the economic viability of mined metals through PM.

## 5. Conclusions and Need for Future Research

While PM holds significant potential, it faces certain limitations, such as the selection of specific plants for certain metals, along with any challenges presented by the formation of the metal compounds in soil. However, PM leverages the natural ability of the plants to accumulate large amounts of valuable metals. It can not only create income for growers but it also provides mineral supplementation and biofuel resources. We indicated that generated income is not improbable; e.g., significant earnings are possible if a yield of 10 t ha<sup>-1</sup> of the hyperaccumulator is combined with an average Ni concentration of 1000 mg kg<sup>-1</sup>. Specifically, economic viability depends on factors like metal content in soil, BAF and TF values of the selected plant species, biomass yields, and metal prices. On the other hand, extensive research remains necessary so that the capabilities and limitations of the PM process may be fully understood. While the majority of the studies have been conducted at the laboratory scale and in a controlled environment for short periods, the true potential of PM awaits investigation at the commercial scale under field conditions for longer periods of time. In addition, interdisciplinary research efforts that combine expertise in different fields of science, such as soil science, plant biology, genetics, and soil chemistry, as well as knowledge of farming practices, are essential for unlocking PM's full potential. Moreover, it is essential to acknowledge that most of the conducted experiments have taken place in developed countries, leaving a knowledge gap for developing nations. We conclude that PM, although a relatively new and unexplored concept, may provide economic and environmental benefits to soil end-users and managers who must cultivate on metal-contaminated soils as PM may turn yield shortages (of specific commercial crops) into benefits if high-yield hyperaccumulators are cultivated for industrial valorization of their high-metal-content biomass. The future of PM should be approached with a balanced perspective, realizing that it may represent a shift in our resource extraction. Phytomining could be the transformative concept whose time has come, provided that we continue to invest in comprehensive research, innovation, and sustainable practices.

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