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Review

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Phytoextraction as a tool for green chemistry

Abstract: The unique chemical and physical properties of metals mean that they are extensively utilized by industry in a huge variety of applications, including electronics, materials, industrial catalysts and chemicals. The increased consumer demand from a growing population worldwide with rising aspirations for a better life has resulted in concerns over the security of supply and accessibility of these valuable elements. As such, there is a growing need to develop alternative methods to recover them from waste repositories, current or historic, both for hazard avoidance and potentially, as a new source of metals for industry. Phytoextraction (the use of plants for the recovery of metals from waste repositories) is a green and novel technique for metal recovery, which, if done with the goal of resource supply rather than hazard mitigation, is termed "phytomining". The ability for plants to form metallic nanoparticles as a consequence of phytoextraction could make the recovered metal ideally suited for utilization in green chemical technologies, such as catalysis. This review focuses on a multidisciplinary approach to elemental sustainability and highlights important aspects of metal lifecycle analysis, metal waste sources (including mine tailings), phytoextraction and potential green chemical applications that may result from the integration of these approaches.

Keywords: elemental sustainability; green chemistry; life cycle assessment; metal recovery; phytoextraction.

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1 Introduction

1.1 Elemental sustainability

Elemental sustainability is a concept in which each element within the periodic table is guaranteed for use by both current and future generations [1]. The long term security of elemental supply has become an important issue at local (industrial), national and continental levels [1]. Elements are not "running out" or being destroyed, but rather are being dispersed throughout the technosphere, making recapture both highly problematic and often costly [2, 3]. These challenges must be tackled through the development of multidisciplinary partnerships, which adopt sustainable, holistic approaches consistent with recovery and reuse [1]. Within this framework, it is also important to consider the triple bottom line of sustainability, i.e., the environmental, societal and economic effects of these elements and their use [4, 5].

Many elements currently have low end-of-life recycling rates, and the overall efficiency of the recycling process is predominately dictated by the collection of waste metal directly after use [6]. Both Pt and Pd already have well-established recycling routes, as their use is dominated by the automobile catalyst industry [1]. Their recovery after use is well understood, and collection is inherent in the current processes for dealing with end-of-life catalytic convertors [7]. This is in contrast to the vast majority of elements which are much more difficult to recycle, due to their low concentrations and dispersion in a wide range of waste streams [7]. By considering the social, economic and environmental impact of an element's life cycle, it is possible to highlight opportunities for the implementation of green and novel technologies for the recovery of elements. Increased rates of recycling will move towards a circular economy and reduce reliance on element extraction and purification [1].

The original source of all metallic elements is mining. New supplies of all industrially important metals must come through the exploration and exploitation of ore bodies. However, recovery of metal from ore is never complete; some metal is residual in waste products generated from the mining industry [8]. Therefore, there exists potential to recover metals from mineral waste materials, as well as from end of life products (recycling) [9]. This review focusses on the potential for living plants to recover metals from waste material, with specific emphasis on the waste generated by the mining industry. The idea that plants can potentially store metal in an active or functionally useful form in living tissues (for exploitation in higher value chemical applications) is central to our review. We therefore place the technology of phytoextraction within the concept of green chemistry and consider the possible implication of using plants to recover metals. Included, is also a discussion of present and possible future uses of this recovered metal, *in situ* within the plant material, in order to show the potential of phytoextraction technology for the provision of novel, sustainable materials, i.e., catalysts.

1.2 Where does phytoextraction fit with elemental sustainability?

Phytoextraction describes the technological use of plants to extract metal from soil and has been extensively developed by academic and industry groups around the world to target industrial waste sites, with the goal of hazard mitigation [10]. Phytoextraction and the associated applications of this technology (phytoremediation, phytodegredation, phytostabilization, phytovolatilization and phytomining) have been reviewed extensively in recent years [10–17]. The purpose of this review is not to re-review phytoextraction. Instead, the technology is proposed here, in the context of elemental sustainability, to be a potential mechanism to recover some industrially relevant metals from waste, particularly from waste generated by the mining industry. The metal content of ore deposits can range from only a few g/ton for the platinum group metals (PGMs) and Au, to % levels for the base metals such as Cu, Pb and Zn. However, the recovery of these metals from rock is challenging and incomplete and the process will generate a significant volume of waste material that still contains metal. Two specific waste products can be defined in the context of mining. The term "waste rock" describes coarse material that is generally stored on surface sites once they are removed from the ground to expose an ore body; while "tailings" describes finely ground material that has been rejected by metal or mineral processing plants [8]. Metal production from these waste materials via phytoextraction could therefore supplement primary global supplies generated by the mining industry and the scenario of targeting strategically important metals using plants with the objective of recovery for industrial use, would be an example of phytomining [18].

The life cycle of a metal in industrial use is shown in Figure 1. The initial stage of mining and processing results in the discard of most of the material that has been mined (the "tailings"). The amount of metal residual in tailings is dependent on the ore and the efficiency of the extraction technology used. Tailings from historical mining operations can have mineable concentrations of metal according to modern-day standards. Subsequent stages of processing also generate losses ("slags"); these are more chemically complex and of much lower volume. Losses during manufacture of products are typically captured and recycled (Figure 1). The result is that there are two life stages where worthwhile recovery opportunities may exist: (1) in the tailings, which are voluminous and in which the metals are often at quite low concentrations, and (2) in the recycling of discarded metal-containing products (Figure 1), which are chemically very complex and are widely dispersed geographically.

The phytoextraction of metals from tailings could contribute to industrial supplies if the recovery from waste materials using plants was economically viable. Mine tailings are regularly reprocessed by classical mining methods, when improved technology enables the tailings to be economically re-mined. In this context, phytoextraction can be considered as a potential reprocessing technology [20]. The economic argument for phytoextraction would be stronger if the presence of metals in plant biomass led to some functionality of the metal in industrial applications relative to bulk metal [21]. But what is the potential global resource inventory for mine tailings

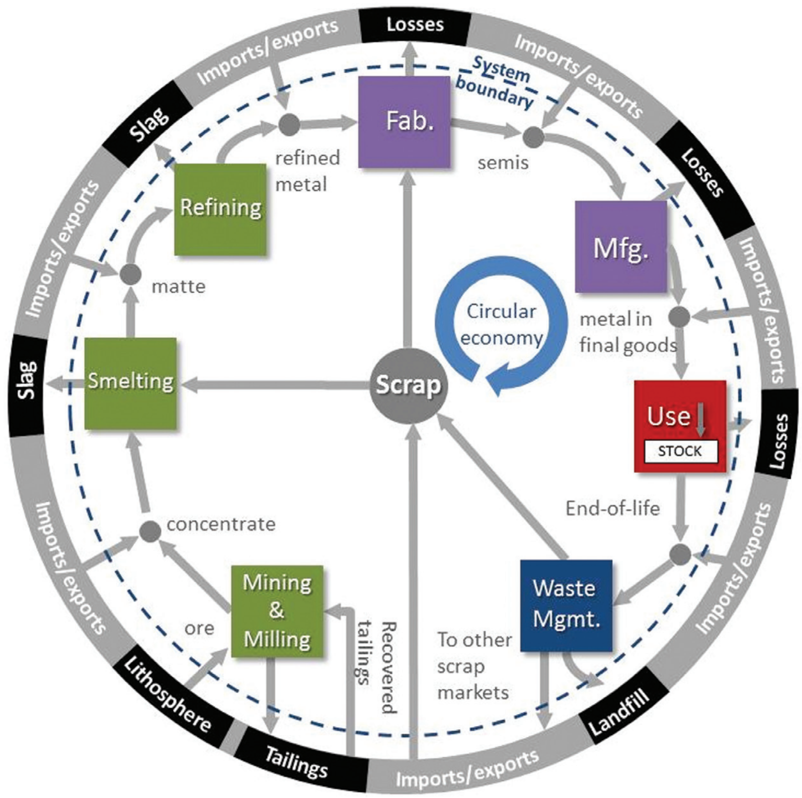

Figure 1 The generic life cycle of a metal. Life cycle stages include mining and milling; smelting; refining; fabricating (Fab.); manufacturing (Mfg.); use; and waste management and recycling (Waste Mgmt.). The dotted line indicates the boundary of analysis, generally a country or region. Between life stages, the grey circles indicate markets that trade the metal in various forms (concentrate, matte, refined metal, semis, metal as a component of a product). Adapted from Reck et al. [19].

that might be amenable to phytoextraction? We propose that phytoextraction resource potential can be quantified on a global basis as follows:

1. Locate all active, inactive or closed mine sites for the metal of interest.
2. Estimate the volume of tailings at each mine site. (This information is sometimes contained in mine-related documents or can be estimated by knowing historic mine production and ore grade.)
3. Determine, by measurement or estimation, the average concentration of the metal of interest in each mine's tailings.
4. Estimate the efficiency of phytomining for the recovery of the metal of interest (will be a function of chemistry, biology and climate).
5. Sum the total recoverable stock of "tailings reserves" in all mines.
6. Compare the total recoverable tailings reserves of the metal of interest with the ore reserves (reserve estimates are generally available, i.e., through the U.S. Geological Survey) [22]. If the former is as much as perhaps one-tenth of the latter, phytomining may have the potential to play a useful part in the provisioning of the metal of interest.

To our knowledge, an evaluation of global reserves of phytomining-exploitable metal has not yet been carried out for any metal, but it would be worthwhile to do so in order to determine whether a significant new resource could be exploited through phytomining for any of the metals used in modern technology.

The elemental recovery rates at the concentration stage are noted in the literature for Fe [23], Cu [24], Ni [3, 25], Pb [26], Zn [27] and the PGMs[28]. Utilizing these values along with historical production statistics from the U.S. Geological Survey [22, 29], it is possible to calculate preliminary estimates of how much metal has cumulatively been lost to tailings for these elements as a percentage of their reserves and reserve base values [22, 30]. The results are displayed in Figure 2.

The values noted here should only be considered as first estimates. There is a great deal of uncertainty not only in the recovery rates, which vary over time with changes in the grade and mineralogical complexity of

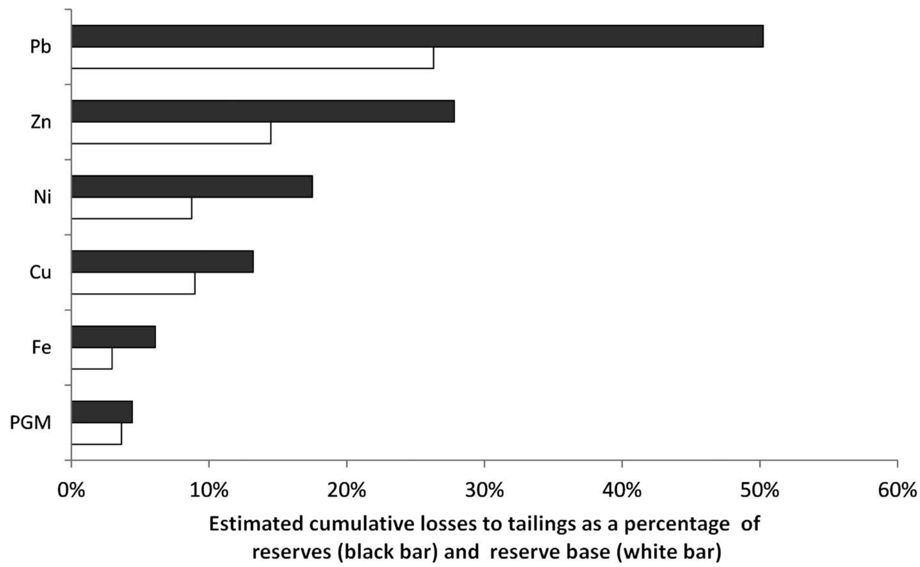

Figure 2 Estimates of cumulative losses to tailings from 1900 to 2012 as a percentage of their latest reserve (black bars) and reserve base (white bars) estimates presented in descending order [platinum group metal (PGM) estimates, excluding other precious metals such as Au and Ag].

the mined ore as well as with technological enhancements, but also with the reserve and reserve base estimates and to a lesser degree, with the production statistics. Furthermore, as some of the tailings may have been reworked, used to backfill mines, utilized as fertilizer or because the low concentration of the metal within the tailings is likely unrecoverable, these values are best regarded as upper bounds of what could potentially be recovered [31]. Nonetheless, the results from this simple analysis suggest that there are significant resources of these elements that have accumulated in tailings over the years.

The elements analyzed here are base and precious metals that are predominantly mined for the sole purpose of their recovery. There are, however, a number of technologically-important elements that are extracted and recovered as by-products of these and other metals. Examples include V, Co, Ga, Ge, Se, Cd, In and Te. These so-called "companion metals" or "hitchhiker elements" may be of importance for phytoextraction, because they are often not recovered or are only recovered at low rates during processing and are thus lost to the tailings or slag of their "host metals".

The provisional calculations presented in Figure 2 describe the scale of the potential global metal resource that could be exploited by phytoextraction. However, the extent to which plants will take up these metals is a function of plant physiology and chemistry. The following section considers practical issues related to metal recovery from these potential reserves.

2 Phytoextraction: exploiting the potential of phytoremediation

Plants and plant-derived biomass have received significant attention from both industry and academia for the production of chemicals and materials [32, 33]. The use of renewable feedstocks for the chemical industry is in close agreement with the principles of green chemistry. Additionally, the associated growth of this biomass has the added advantage that it might aid in reducing climate change through the fixation of CO_2 [34]. However, the ability of plants to accumulate inorganic species for extractive value has received relatively less attention and is yet to be fully exploited [35, 36].

Any application of phytoextraction requires plants that have the following attributes: fast growth rates, high biomass composition, deep roots, tolerance to metal uptake, metal specificity and a high rate of metal transport from roots to shoots [34, 37]. During phytoextraction, uptake occurs through the plant root system [38, 39]. Optimal efficiency is achieved by using plants that can readily translocate contaminants from roots and accumulate these in shoots. Shoot biomass can then be harvested and processed to recover value from the crop [40, 41]. When applied to metal recovery from wastes, phytoextraction can potentially lead to two revenue streams: (1) environmental clean-up and (2) valuable metal products. A significant number of studies have investigated the use of phytoextraction to recover metals released into the environment by anthropogenic activities and industrial processes, using both hyperaccumulator and non-hyperaccumulator species; some examples are given in Table 1. Many of the practical phytoextraction examples use non-hyperaccumulator species, due to the higher biomass production of these plants compared to hyperaccumulators. Section 4 of this paper goes into more detail about practical phytoextraction scenarios.

3 Plant strategies for growth in contaminated soils

Plants exhibit one of three strategies in response to the presence of metals in soil. Plants expressing these responses were defined seperately by Van Der Ent et al. and Baker and Walker as metal excluders, metal indicators or metal accumulators (hyperaccumulators) [53, 54].

Metal excluders avoid importing metals to aerial organs, however, they may still contain relatively high amounts of metals in roots (Figure 3) [56]. Boularbah et al. [57] defined an excluder as a plant species that can have high levels of heavy metals in the roots, but always has a shoot/root quotient of less than one. *Salix* (willow) species are examples of metal excluders.

Metal indicators accumulate metals in above ground tissues to levels similar to those in the surrounding soil [55]. The relationship between the concentration of metal in the plant and soil is generally linear (Figure 3). Metal indicator plants have received attention since the late 1800s as metal accumulator plants [58]. A recent example demonstrates the potential use of Eucalyptus trees, which translocate Au from deep (>10 m) mineral deposits to their aerial tissues, to identify Au deposits [59].

The concept of *metal hyperaccumulator* plants was first described for nickel accumulating species by Jaffré et al. [60]. The definition of hyperaccumulation has been refined a number of times and was most recently updated by van der Ent et al. in 2013 [53]. The current definition for a hyperaccumulator can be summarized, for nickel, as a species that, when growing in its natural environment accumulates at least 1000 mg/kg nickel (dry weight) within its leaves. Hyperaccumulator species that concentrate other elements, including Zn, Cd, Pb, Co, Mn, Cr and Se have also been identified, and hyperaccumulation threshold limits have been established for each metal, for example, 100 mg/kg (e.g., Cd), 1000 mg/kg (e.g., Pb) or 10,000 mg/kg (e.g., Mn) of metal (Figure 4) [53].

Baker et al. [62] first postulated the use of hyperaccumulator species in phytoremediation (phytoextraction), because these plants are potentially capable of accumulating an exponentially higher concentration of certain elements relative to that which is in the surrounding soil.

Table 1 Practical phytoextraction examples by hyperaccumulator and non-hyperaccumulator plants.

Practical scenarios	Location	Metals	Plants	References
Soil contaminated by metal-bearing sewage sludge	UK	Cd, Cu, Ni & Zn	20 Varieties of *Salix*	[42]
		Ni & Zn	*N. caerulescens*	[43]
	Switzerland (Ziefen)	Cd	*A. murale*, *N. caerulescens*, *S. viminalis*	[44]
	Switzerland (Caslano)	Cd & Zn	*N. caerulescens*, *S. viminalis*	[45, 46]
	United States	Zn & Cd	*N. caerulescens*, *S. vulgaris*	[47]
	Malaysia	Al, Cu, Fe & Zn	*J. gendarussa*	[48]
	France, UK, Germany, Sweden	Cd & Zn	*N. caerulescens*	[49]
Soils contaminated by different smelters	France, Sweden, UK	Cd & Zn	*N. caerulescens*	[49]
	Switzerland (Dornach)	Cd & Zn	*A. murale*, *N. caerulescens*, *S. viminalis*	[44] [45, 46]
Ni refinery	Canada	Co & Ni	*A. murale*, *A. corsicum*	[50]
Contaminated paddy fields	Japan	Cd	*O. sativa* (MORETSU and IR-8)	[51]
			H. cannabinus	[52]

A.=Alyssum; H.=Hibiscus; J.=Justicia; N.=Noccaea; O.=Oryza; S (viminalis)=Salix; S (vulgaris)=Silene.

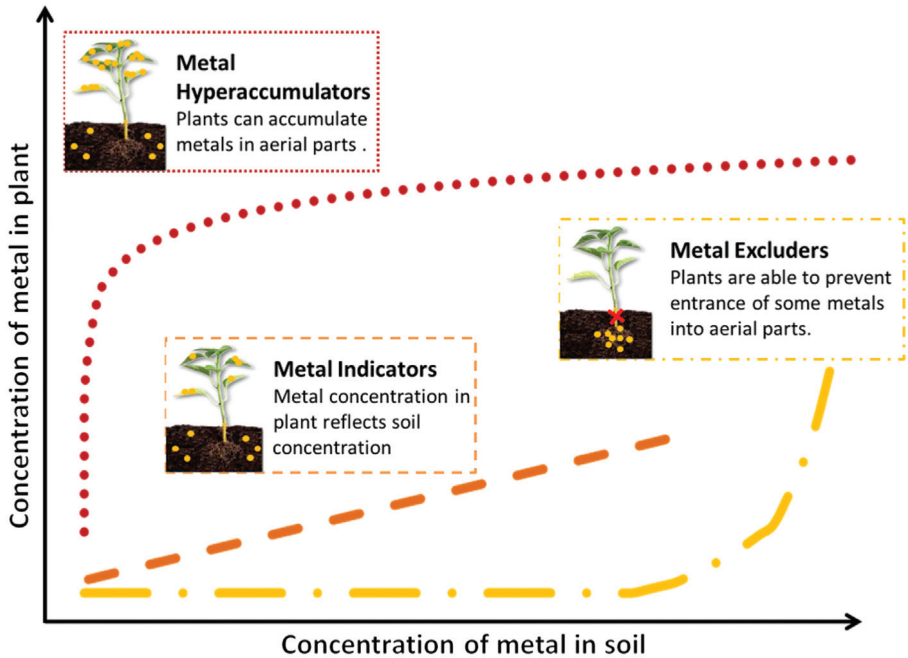

Figure 3 Three response strategies of plants to an increasing metal concentration in soil: hyperaccumulation (red line), metal indication (orange line) and exclusion (yellow line) [55].

3.1 Use of hyperaccumulator species for phytomining

In recent decades, many hyperaccumulator species have been investigated for the clean-up of soil and water [9]. Table 2 summarizes a range of known hyperaccumulator species and describes the number of metals that are known to be taken up. Many elements highlighted within Table 2 have been classified as critical elements (which are vital for a company's, nation's or continent's business/economy and also have significant potential for a restricted supply) [1]. Co has been highlighted as a critical element of global importance, Mn and Ni are of multinational importance and Cr, As, Cu, Tl and Cd are of national importance [1]. This highlights the great potential for utilizing phytoextraction in terms of elemental security and sustainability [1].

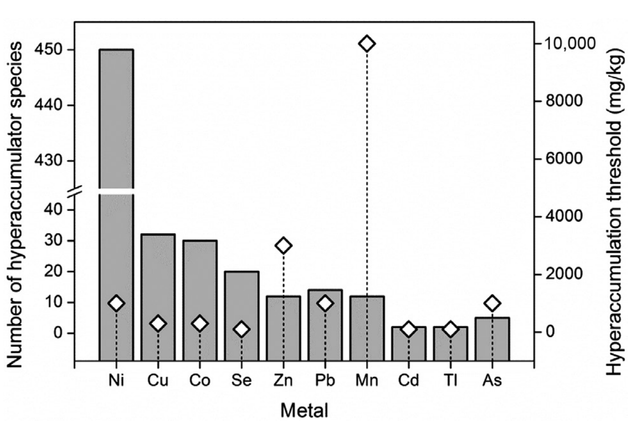

Figure 4 Number of species identified as hyperaccumulators and the hyperaccumulation threshold [53, 61].

A more detailed review of Ni hyperaccumulators has recently been reported by Jaffré et al. [84]. The Brassicaceae family is of particular interest, as it contains approximately 25% of the known Ni hyperaccumulator species, along with species that accumulate Zn and Cd [85]. Within this family, the Zn and Cd hyperaccumulating species *Arabidopsis halleri* (*A. halleri*) and *Noccaea caerulescens* (*N. caerulescens*, formerly *Thlaspi caerulescens*) share close phylogenetic links with *Arabidopsis thaliana* (*A. thaliana*), a model species for molecular genetics. As a result, much of the current knowledge on the molecular mechanisms behind hyperaccumulation has been elucidated from *A. halleri* and *N. caerulescens*.

When compared to crop species, hyperaccumulator species generally have low growth rates and poor biomass accumulation. Over a number of years, Chaney and co-workers [15], in collaboration with the US company Viridian Resources LLC, collected *Alyssum* species, predominantly from the Mediterranean area, and rigorously analyzed for Ni phytomining potential. These species were then selectively bred to obtain varieties with improved agronomic traits for Ni phytomining in the field. Promising results from these efforts were achieved with *Alyssum*

Table 2 Distribution of known metal accumulator species to plant families.

Family	Genus	Species	Metals in plants (mg/kg)	Metals in soil (mg/kg)	References
Amaranthaceae	*Alternanthera*	*sessilis*	Fe 2120.4, Cr 749.3	Fe 38000, Cr 100[a]	[63]
Asteraceae	*Baccharis*	*sarothroides*	Cu 1214.1	Cu 529.6	[64]
	Berkheya	*coddii*	Ni 7880	Varies	[65]
	Chichorium	*intybus*	Pb 1141.5	Pb 500	[66]
Brassicaceae	*Alyssum*	*bertolonii*	Ni 1.83%[b]	Ni 0.16%	[67]
	Alyssum	Various species	Ni[c]	–	[68]
	Iberis	*intermedia*	Tl 2810	Tl 14	[69]
	Arabidopsis	*halleri*	Cd 82.3[d]	Cd 956	[70]
	Streptanthus	*polygaloides*	Ni 14800	Ni 3840	[71]
	Noccaea	Various species	Pb 8200, Zn 17300	Pb 0.3%, Zn 1.7%[b]	[72]
	Haumaniastrum	*robertii*	Co 10222	Up to 10%[b]	[73]
	Cynodon	*dactylon*	Fe 1150.4, Cr 740.0	Fe 38000, Cr 100	[63]
	Ricinus	*communis*	Pb 2029[d]	Pb 2267	[74]
Buxaceae	*Buxus*	Various species	Ni[c]	–	[75]
Cunoniaceae	*Geissois*	Various species	Ni[c]	–	[76]
Euphorbiaceae	*Leucocroton*	Various species	Ni[c]	–	[75]
	Tephrosia	*candida*	Pb 1689[d]	Pb 2207	[74]
Fabaceae	*Homalium*	Various species	Ni[c]	–	
Phyllanthaceae	*Phyllanthus*	Various species	Ni[c]	–	[75]
Proteaceae	*Beaupreopsis*	*paniculata*	Mn 12000	–	[77]
	Macadamia	*angustifolia*	Mn 12589	–	[77]
		neurophylla	Mn 55200	Mn 4800	[77]
Rubiaceae	*Psychotria*	*douarrei*	Ni 4.7%[b]	Ni 0.37%	[78]
Salicaceae	*Casearia*	*melistaurum*	Ni 1490	–	[79]
Salicaceae	*Lasiochlamys*	*peltata*	Ni 1000[d]	–	[79]
Salicaceae	*Solanum*	*photeinocarpum*	Cd	100	[80]
	Xylosma	Various species	Ni[c]	–	[79]
Sapotaceae	*Pycnandra*	*acuminata*	Ni 1.17%[b]	0.85	[60]
Violaceae	*Hybanthus*	Various species	Ni[c]	–	[81]
	Rinorea	*bengalensis*	Ni 17500	–	[82]
	Rinorea	*javanica*	Ni 2170	–	[83]

[a]Typical background concentration in soil (mg/kg).
[b]The data is expressed by % of dry matter.
[c]When several species belonging to same genus are discussed, metal concentrations are not shown in the table.
[d]The data displayed in the table correspond to the highest concentrations of metal in soil and plants, with the exception of these highlighted exceptions.

murale (*A. murale*) cultivars grown in serpentine soils in Southern Oregon [86], but in a similar study in Sulawesi, Indonesia, the same species performed poorly, apparently because this temperate species was unable to adapt to the higher temperatures found in tropical environments. These observations bring into the spotlight the current debate on the use of non-native species for phytomining. With *A. murale* and *Alyssum corsicum* (*A. corsicum*), both native to the Mediterranean region, now listed as invasive species by the Oregon Invasive Species Council [87], researchers are pursuing the use of local species whenever possible. These species are more likely to be better adapted to the local environment, and comply with local legislation restricting the use of invasive species [1]. Furthermore, field experiments in Indonesia are hoping to ally phytomining alongside the conservation of native hyperaccumulator species and erosion control as part of a rehabilitation strategy for large areas of, currently unvegetated, mined land [88].

3.2 Use of non-hyperaccumulator species for phytomining

A number of studies have investigated the use of non-hyperaccumulating species to take up metals. While some of these studies have contributed greatly towards the understanding of metal uptake, non-hyperaccumulating species are not generally considered suitable for phytomining [89]. In particular, the use of food crop species to phytomine high levels of potentially toxic metals is questionable.

However, there are advantages to using specific, non-food crop, non-hyperaccumulating species. For example, some *Salix* and *Populus* species, although not hyperaccumulators, are high biomass producers and are able to accumulate high levels of Cd and Zn [90]. Additionally, there are existing biomass harvesting methodologies and machineries in use for these crops. These species thrive in a broad range of environments where suitable hyperaccumulator species are not always able to grow.

3.3 Chemically assisted or induced phytoextraction

Attempts have been made to enhance metal uptake by plants for remediation through application of chemicals to soil and this is known as assisted or induced phytoextraction. This technique employs metal chelators, such as ethylenediaminetetraacetic acid (EDTA), N-hydroxyethyl-EDTA (HEDTA) or citric acid in an attempt to increase the metal uptake capacity and the translocation of metals inside plants from high biomass species (Table 3) [93, 102, 103, 104]. The use of EDTA for assisted phytoextraction has been widely studied in the past [105]. Huang et al. [99] found that an increase in Pb uptake in shoots from 50 mg/kg to up to 11,000 mg/kg of *Pisum sativum* was achieved after EDTA addition. The efficacy of induced hyperaccumulation to target metals that are not hyperaccumulated by plants is a function of the geochemistry of metals in soil; induced hyperaccumulation relies on the formation of a stable metal chelate or ligand complex in soil solution. The induced hyperaccumulation of Au has been extensively reported in literature using chemicals such as thiocyanate, thiosulfate or cyanide [91]. Precedent for the induced hyperaccumulation of precious metals therefore opens up the possibility of employing phytoextraction for the recovery of the industrially more important PGMs from mine waste [99].

However, questions have been raised about the introduction of chemicals like EDTA into the environment. EDTA presents a low biodegradability rate and could therefore be considered as a persistent organic pollutant. There is also the added disadvantage that metals that were previously bound to the soil become free in the environment, with no guarantee that this freely available metal will all be successfully phytoextracted by the plants. This leads to the risk of groundwater pollution by leached metal complexes [106]. Given these issues, the use of EDTA is no longer considered to be a responsible choice for increasing metal uptake and new alternatives are being developed [102]. The potential risks on the use of cyanide during Au phytomining were recently reviewed and discussed by Anderson [61] and Wilson-Corral et al. [91].

Natural, low molecular weight organic acids (NLMWOA) have been tested as alternative chelators to EDTA, due to their fast biodegradability rate [107]. Some examples of NLMWOA are citric acid, oxalic acid or vanillic acid [93]. Unfortunately, these chemicals can rapidly biodegrade, often resulting in breakdown before the metals are absorbed by the plants [93]. Ethylenediaminedisuccinic acid (EDDS) is another alternative chelator to EDTA. It biodegrades faster and has been proven to enhance Cu and Zn uptake when applied to contaminated soils [92]. However, further investigation is required in this area to find an alternative that offers the same results as EDTA. The use of chelates in phytoextraction often requires specific risk assessments associated with the individual site; such activities can be costly, time consuming and may require legislative approval. Although chelates have been used to aid phytoextraction and increase metal recovery, such activities can have a negative environmental impact. There are still opportunities for green chemical

Table 3 Examples of induced hyperaccumulation.

Families	Species	Metals	Amendment	References
Asteraceae	*Helianthus annuus*	Cu & Zn	EDDS	[91, 92]
Brassicaceae	*Brassica juncea*	Cd, Cu, Ni, Pb & Zn	Gallic and citric acid	[93]
		Cd, Cu, Ni, Pb & Zn	EDTA	[94]
		Cd	Citric acid and NTA	[95]
		Au, Ag	NH_4SCN	[96, 97]
Various	*Various*	Cd	NTA	[98]
Fabaceae	*Pisum sativum*	Pb	EDTA & HEDTA	[99]
Poaceae	*Lolium perenne*	Cr, Ni & Zn	EDTA	[100]
	Phalaris arundincacea	Cr	EDTA	[100]
	Zea mays	Zn	NTA	[101]

technologies to be developed that increase the availabilities of elements to plants without having a detrimental effect on the environment.

3.4 Bioengineering to improve phytoextraction

Compared to many agricultural practices, phytomining is very much in its infancy. Despite the obvious abundance of hyperaccumulator species with phytomining potential, only a few species have the required agronomic traits for successful phytomining. Improving the poor agronomic traits, such as yield, growth rate, plant architecture and biomass production, commonly found in hyperaccumulator species, requires the transfer of numerous genes, and is perhaps best left to more traditional plant breeding and quantum trait loci-based mapping techniques. At present, if the environmental conditions concur with those of a selectively bred, hyperaccumulator, such as an *Alyssum* cultivar, then this could be the only current, commercially viable method of phytomining the majority of field sites. For sites where *Alyssum* species are not native or environmental conditions are unsuitable, alternative candidate native species need to be identified and selective breeding programs urgently established.

Studies to understand, at the genetic level, metal uptake and translocation by hyperaccumulator plants have been progressing for over a decade. At the molecular level, comparative studies have been successfully used to identify candidate genes. For example, experiments comparing the transcriptome of the hyperaccumulator *A. halleri* with the closely related *A. thaliana*, have identified over 30 candidate genes that are expressed at higher levels in *A. halleri* than in *A. thaliana* [108, 109]. Many of the genes implicated in metal hyperaccumulation are transporters, and not just at the soil root interface; transporters expressed at specific cell and organelle levels from the root plasma membrane all the way up to organelle membranes in the aerial plants play major roles in metal uptake and translocation [110, 111]. In addition to transporters, metal-complexing ligands, such as metallothioneins and phytochelatins have been shown to be involved, and genes from non-plant organisms have also been employed. The major breakthroughs in engineering hyperaccumulation phenotypes into non-hyperaccumulator species include: The expression of heavy metal ATPase 4 from the hyperaccumulator, *A. halleri*, in *A. thaliana* resulting in conferred resistance to Cd and Zn [112]. Tolerance to, and accumulation of, As was enhanced in *A. thaliana* by combining expression of a bacterial arsenate reductase, in tandem with a gamma-glutamylcysteine synthetase [113]. Expression of bacterial *merA* and *merB* genes in *A. thaliana* conferred resistance to mercury, and rather than hyperaccumulation, volatilization of elemental mercury [114]. Advances in genome sequencing are also adding to the number of known genes from previously uncharacterized hyperaccumulator species.

The knowledge gained from experiments on species used as models for molecular biology is being transferred into plant species that are more amenable to phytoremediation. For example, the studies outlined above have now been progressed into *Populus* [115–117]. Nevertheless, factors such as the lack of transformation protocols, the slow regeneration time for many of these species and, in many countries, restrictive regulatory rules governing the testing of genetically modified plants in field trials are limiting progress. In addition, individual studies on many other candidate genes found that, when expressed, they failed to improve tolerance or metal accumulation [118], and there is still much scientific research needed to successfully harness the enormous potential of this technology.

4 Real strategies for phytoextraction

The process of mining involves removal of vast amounts of material that covers the actual ore body. Once the ore body is reached, mining for the target commodity can commence. Where the target is metal, the mined ore is ground to a particle size that liberates valuable minerals from non-valuable components (gangue) generating a concentrate that can be smelted and refined. The ground-up waste material is called tailings and this must be safely stored within a purpose-built facility. Both tailings and the coarser waste material contain a range of residual metal and non-metal components, some of which may have residual values that are potential targets for phytoextraction (phytomining).

However, waste rock and tailings are not the only possible mining resources that can be exploited by phytoextraction. Slags and residues formed during the smelting of the concentrate and during the refining of the impure valuable metal from the smelter are also potential phytoextraction targets. In most cases, concentrate and smelter wastes are recycled; however, phytoextraction may represent a viable reprocessing technology if a higher value product can be generated.

4.1 Practical phytomining scenario: phytoextraction of metal from tailings

Mine waste is generally stored in dams or piles that, in the past, were often poorly constructed and still are today at artisanal or small-scale mine sites [119]. They represent an edaphically challenging environment for plant growth. In addition, the dumps and storage facilities are deep (of the order of tens of meters) and in some parts of the world, the availability of flat land constrains the area of a storage facility. This is again particularly true at artisanal and small-scale mining sites where tailings can contain a high level concentration of valuable metals due to inefficient process technology [120]. Exploitation of the entire tailings volume using plants would be impractical, due to the physical limits of plant growth and rooting depth. If a phytoextraction operation is to proceed, the pile could be re-mined and then spread out on a new site at a reduced height in order to create sequential horizons of tailings or waste rock that can be exploited by plant roots (up to 1.5 m). There are two scenarios to achieve this result (Figure 5):

1. Phytoextraction could be implemented on the surface material of the original dump *before* the top layer is stripped off to begin construction of a safe storage facility elsewhere. This process would continue until all the material has been treated and moved to the new site. Figure 5A graphically depicts several stages of operation for an example four-lift dump.
2. Alternatively, phytoextraction could be implemented on the first layer *after* removal and placement in a new storage area. Following exhaustion of the resource, more material is placed on top of the original layer and the process continues until all material has been transferred to the new site. Figure 5B graphically displays the various stages of this scenario.

Different sites will require different design approaches. Scenario A causes no additional land disturbance, since the new site is equal in size to the original site which is reclaimed. For Scenario B, there is potential to increase the footprint of the tailings pile through spreading the waste material over a larger area relative to the original pile. Increasing the footprint of the "phytomine" in Scenario B would lead to a greater rate of metal recovery relative to Scenario A.

Phytomining in both scenarios has potential to contribute to the reclamation or rehabilitation of tailings storage facilities. The sequential recovery of value from mine waste prior to removal of this material to a new site, or from the waste after is has been moved to a new site, could generate revenue that can subsidize the costs of environmental clean-up at sites that require physical intervention to produce a more-stable dam structure. The scenarios described in Figure 5 differ with respect to the scheduling and integration of phytomining with reclamation. A bottom-up approach will prepare the material in a way that may enhance the availability of metal for phytoextraction and will increase the overall extraction rate. A key issue, however, will be the trade-off of extraction rate vs. land area.

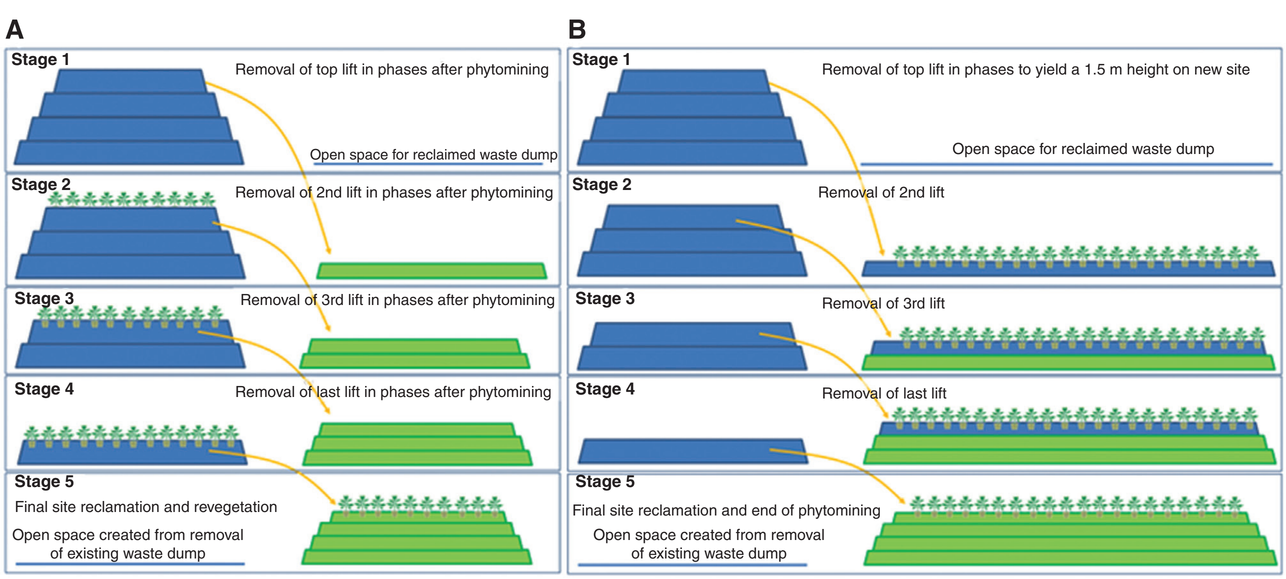

Figure 5 Phytoextraction of mine tailings (A) top-down approach and (B) bottom-up approach.

4.2 Possible limitations and risks to be considered

Phytoextraction is an attractive tool for the recovery of metals. However, potential limitations and risks should be considered when employing phytoextraction and these concerns should be considered during the design of any operation. A principle concern is the slow growth rates of plants and therefore, the low rate of production compared to mechanical methods [121, 122].

Low biomass production by metal-hyperaccumulating plants can limit the effectiveness of the large-scale decontamination of a site where effectiveness is dependent on the harvested biomass and metal accumulation by dry matter (although the available number of hyperaccumulator species for Ni is an exception to this limitation) [34, 121]. Limited biomass leads to economic concern about the process, since it may take a long time for a crop to accumulate enough metal to recover the initial costs of planting and harvesting.

The growth of all plant species (hyperaccumulator or non-hyperaccumulator) can be limited by soil environments with physical or chemical properties that inhibit biomass production [123]. For example, the fine particle size of tailings results in a growth media that has limited porosity and therefore, limited oxygen content and potential for drainage. Anoxic conditions associated with such soils are not conducive to plant growth. Chemical impediments can manifest through the presence of potentially phytotoxic elements such as Cu, Cd and As that exist within mineralized ore [124, 125]. If these elements are not recovered from the ore during processing, then the tailings will also have a high concentration that can detrimentally affect plant growth. Many essential nutrient parameters are limited in waste rock or tailings. In particular, the organic C and N status of mineralized rock is generally very low, and organic nutrient content is essential for microbiological soil health and nutrient cycling. These are important parameters for plant growth.

Phytoremediation is limited by the depth that plant roots can reach, and is generally restricted to shallow (< approximately 2 m) soils. Therefore, only surface contaminants can be removed unless sequential stripping is performed to allow the plants access to subsurface metals. Sequential stripping is likely to increase the cost of the process. Other limitations include climatic and geological conditions of polluted target area, such as; temperature, altitude and the accessibility of the site by necessary agricultural equipment and labor [126]. Van der Ent et al. [88] recently described the failure of large scale phytomining of ultramafic soil in Sulawesi, Indonesia, due to the inability of the temperate species used in this work to grow in a tropical environment.

Environmental concerns include the potential for metals to enter trophic chains via herbivory of metal-containing biomass [121]. There are also problems with the treatment and disposal of harvested metal-containing biomass, as this must be handled as a hazardous waste [55]. The introduction of non-native plant species to a recovery site, as discussed in Sections 3.1 and 3.4, could also be a problem, since there are potential issues with local biodiversity [55].

Constraints on phytoextraction are not, however, limited to plants and the environment. Resource issues must also be considered. For phytoextraction to be a mechanism to recover metals for industrial application, resource containing this issue must first be secured for operation. Fluctuations in metal prices change the status of mine waste from waste to reserve [18]. The increasing gold price since the late 1990s illustrates this well; tailings from a gold mine in 1998 may be considered a resource in 2013 [22, 96]. Improvements in process technology can also lead to the reclassification of mine waste over time. The ability of a phytomining project to secure access to resource is an issue that must be considered, and represents a potential impediment to project development.

4.3 Sustainability of Au phytomining with time

Anderson [61] recently reviewed commentary on the theoretical number of sequential cropping of Au that could be economically recovered from a piece of land. Sustainability modelling was first described for Ni using the hyperaccumulator *Berkheya coddii* [127], and this subject has been explored by several studies into the economics of phytomining since the original (very rough) economic assessment of Ni phytomining in 1995 [15, 91, 128]. As plant roots do not contact the entire soil volume, plants cannot be expected to recover the full metal loading of the soil in one crop. In the context of Au phytomining, the Au concentration in plants is proportional to the concentration of Au in soil. Under optimal conditions, only 15–20% of the Au content of the root zone would be recovered by plants in any single crop [58]. Recovery at this rate establishes a diminishing metal concentration in plants, as each subsequent crop is extracting Au from soil with a decreased Au concentration. The relationship between diminishing Au concentration in planted ore and the crop is depicted in Figure 6. This model assumes Au phytomining is conducted on waste with a relatively high Au concentration (2 g/ton).

Under optimal conditions, the modeled initial Au concentration in plants that can be expected is 225 mg/kg, and represents recovery of 15% of the total Au in the root

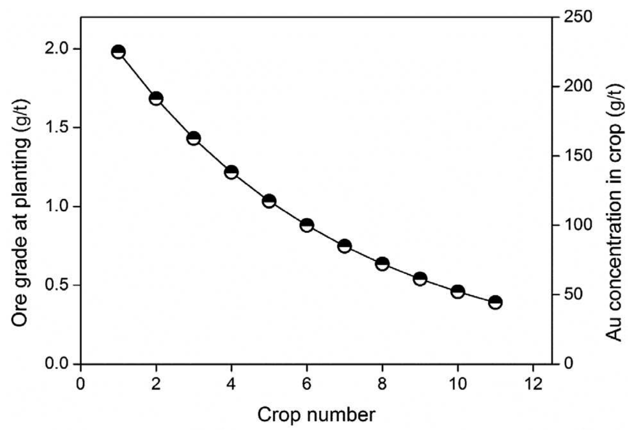

Figure 6 Modelled relationship between successive crop number and Au concentration in ore grade at the time of planting and the Au concentration in crop at the time of harvesting.

zone of a crop of plants (10 ton/ha harvested dry biomass, 50 cm rooting depth and bulk density of the waste of 1.5 ton/m^3). Based on this level of metal recovery, the Au concentration in the ore for the second crop is reduced, and the corresponding Au concentration in the harvested biomass of the second crop is also reduced relative to that in the first crop. Robinson et al. [127] presented a similar decay curve calculation for Ni.

At some point, the concentration of Au in the biomass that can be recovered through phytomining will no longer cover the costs of the operation. Based on current economic parameters, this may occur at Au concentrations in tailings of 1 g/ton [129]. Therefore, for the model in Figure 6, perhaps five crops could be harvested from the same piece of land before the phytomining operation is no longer economically viable.

A cut-off grade of 1 g/ton immediately discounts the applicability of Au phytomining to large volumes of waste around the world; the large tailings dams associated with modern Au mines will all have Au concentrations much <1 g/t. This level of Au can, in fact, be economically recovered by modern mechanical and chemical processing methods mines, assuming the size of the resource is sufficient. The real potential of phytomining, therefore, may be limited to small deposits of high-grade tailings or mineralized soil that do not meet the reserve requirements of the conventional mining industry. There may also be some artisanal mine sites in developing countries around the world that have gold (and other precious metal) concentrations in tailings that make phytomining feasible [61].

It is important to note that the sustainability model described in Figure 6 has not been examined in the field. No phytomining operation for any metal has been described that has involved successive crop cycles of a block of land. The model presented describes the sustainability of Au recovery over time and is reliant on continued induced hyperaccumulation to achieve the target levels of Au uptake. The model is theoretically applicable to the induced uptake of other precious metals, such as Pd and Pt, which require similar chemicals to mobilize the metals.

5 Utilization of phytoextracted metals

Phytoextraction of metals offers three key benefits: (1) decontamination of land, (2) exploitation of more widely-dispersed resources of surface metals and (3) recovery of metals from ore bodies with low metal concentration (e.g., for Ni ore concentration of <30 g/kg can be considered uneconomical) [86]. This concentration of metals from below ground to above-ground into biomass creates the potential for recovery and recycling of the metal for a variety of different applications (Figure 7).

The utilization of phytoextraction technologies in the recovery of elements from marginal mining sites or tailing could be important for the development of a circular economy and also from an elemental sustainability stand point. The most common method used to recover metals from biomass is to treat the biomass as “bio-ore” and extract the metals using conventional processing methods [130]. However, this approach limits the applications and economic viability of phytoextraction [86].

Research has demonstrated that some plant-sequestered metals are stored as pure metallic nanoparticles within the biomass, offering a third key benefit to the use of phytoextraction for metal uptake [97, 131]. Nanoparticles (sometimes called giant clusters, nanoclusters or colloids) [132], are defined as particles with at least one dimension that is between 1 and 100 nm and with properties that are not shared by the bulk of the same metal, e.g., large surface area to volume ratio, high catalytic efficiency and strong adsorption ability [133–136]. These properties of nanoparticles are of significant importance to many scientific fields [137, 138]. The effective use of nanoparticles synthesized within living plants may represent added economic value to the natural phenomenon of phytoextraction.

The extraction of plant-synthesized nanoparticles prior to their use in applications has been attempted using methods such as freeze-thawing, biomass incineration and chemical leaching [139]. However, these activities are laborious, costly, energy intensive, and can destroy the metallic nanoparticle structure, thus interfering with the desired nano-material properties [140]. As a result

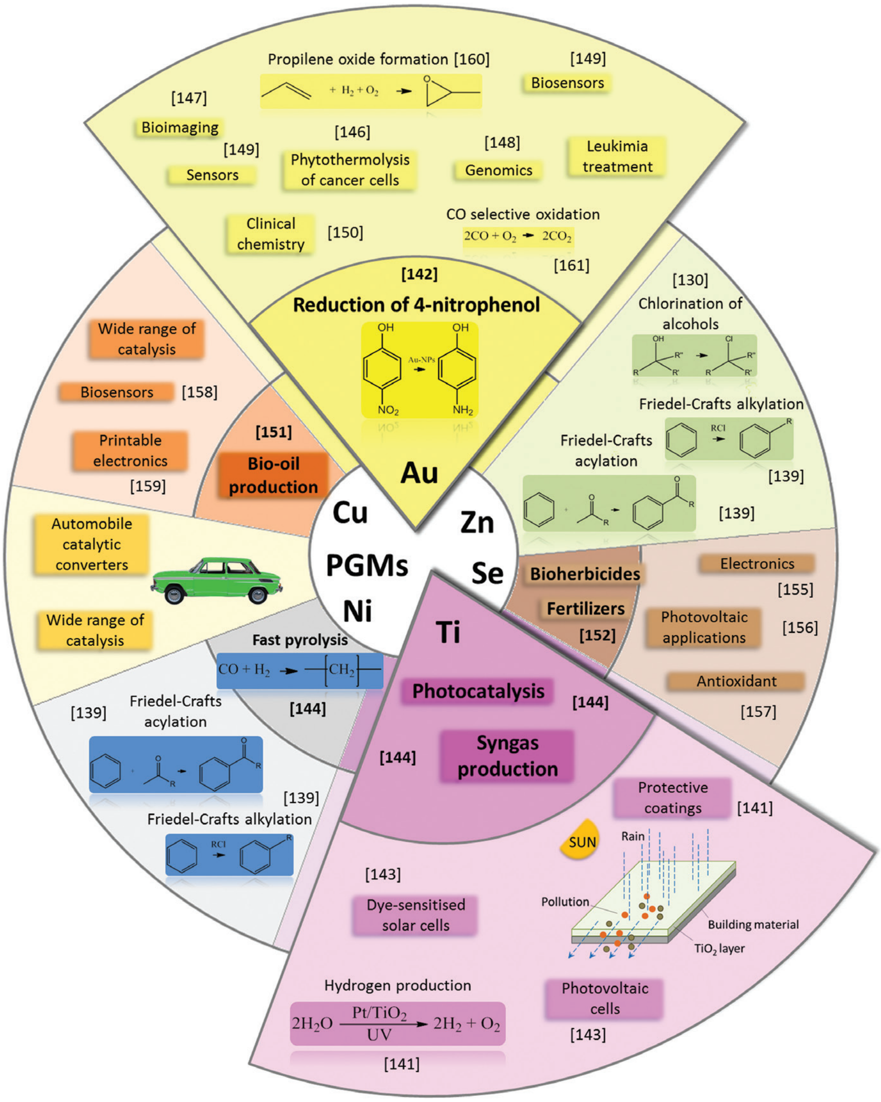

Figure 7 Potential applications of phytoextracted plant material and metals (inner circle in bold: current tested applications, outer circle: future suggested applications).

investigations into the *in situ* use of nanoparticles within the biomass are rapidly gaining interest.

Figure 7 shows a range of metals that have been successfully phytoextracted. The *in situ* use of the metal within the biomass for a range of potential applications is also shown, along with suggestions for other potential future applications. The proven and potential uses of these materials are discussed in more detail below.

5.1 Environmentally relevant catalysis

Catalysis is the central field of nanoscience and nanotechnology [132]. Metallic nanoparticles from across the periodic table have been tested for activity in a range of chemical reactions with great success [132]. Some studies have used plant synthesized Zn and Ni nanoparticles as catalysts for the chlorination of alcohols and Friedel-Crafts chemistry [130, 139]. In these studies, the plant material has first been ashed and the metal extracted prior to use as a catalyst. Although activity is apparent, the ashing process could lead to nanoparticle agglomeration and a reduction in activity relative to full potential.

The application of plant-synthesized nanoparticles to environmentally-relevant catalytic reactions could be an exciting, value-added application for "phytomined" metals. In this field, the unique properties of nanoparticles enable reactions that were not possible or significantly low yielding when using conventional catalysts [141]. Plant synthesized Au nanoparticles have offered exciting possibilities in catalysis for pollution reduction. For example, Sharma et al. [142] carried out a study into the uptake of Au by *Sesbania drummondii* seedlings. The Au nanoparticles were shown to be effective catalysts for the reduction of the pollutant 4-nitrophenol without extraction of the nanoparticles from the plant.

Titanium dioxide (TiO_2) nanoparticles are another important material for environmentally relevant catalysis. Work has demonstrated that TiO_2 nanoparticles are excellent catalysts for applications including photocatalysis, dye-sensitized solar cells and photovoltaic cells [143]. While bulk TiO_2 is relatively non-conducting and therefore ineffective in these processes, efficient electron transport is achieved through the large surface area of nanoparticles [141]. Mahmood et al. [144] have shown the potential for use of plant synthesized TiO_2 nanoparticles, formed by phytoextraction using water hyacinth, as effective photocatalysts for the production of syngas. This work may lead to other applications of plant-synthesized TiO_2 nanoparticles, for example, in the production of hydrogen by the photolytic dissociation of water, where TiO_2 continues to be the most promising material for use in this area [141].

The most well-known use of nanoparticles for environmentally relevant catalysis is the utilization of Pt, Pd or Rh nanoparticles (or mixtures thereof) in automobile catalytic converters. Catalytic converters in various forms have been used for nearly 40 years for scrubbing exhaust gases and today are an integral part of emission control [145]. However, the PGMs are a finite resource. Their leaching from automobile catalysts during use, leads to the subsequent inclusion of PGMs in roadside dust; in addition to the existence of these metals in mine waste or in small deposits of mineralized rock, all represent potential resources that might be exploitable by phytoextraction. The conversion of plants containing metals into heterogeneous catalysts could lead to retaining the activity of nanoparticles, thus providing a green method for the utilization of these high value materials.

5.2 Biomedical applications

The use of nanoparticles for biomedical applications is a heavily researched area. This is especially true in the case of Au nanoparticles, where the ever increasing diversity of published applications includes biosensors, genomics, clinical chemistry, photothermolysis of cancer cells and tumors, targeted drug delivery and optical bioimaging of cells and tissues [146–150]. Whilst no examples of plant-synthesized nanoparticles being used in biomedical applications are currently reported, a greener route for their synthesis could potentially increase the safety of nanoparticle manufacture. Increased safety could be afforded through the elimination of toxic chemicals often used in conventional nanoparticle synthesis techniques [21].

5.3 Other

Other, lower value uses of biomass containing phytoextracted metals have been proposed. For example, biomass containing Cu (as a catalyst) has proven useful in the improvement of bio-oil quality produced through fast-pyrolysis of biomass [151]. The Cu in Cu-enriched biomass effectively catalyzed the thermo-decomposition of the biomass and resulted in an improvement in the yield and heating value of the bio-oil compared with non-Cu containing biomass [151]. Cu did not volatilize during treatment and this prevented metal contamination of the bio-oil.

Research is also being carried out into the use of Se-containing plants for a number of applications, such as fortified foods, biofuels or potential bioherbicides and green fertilizers [152–154]. For example, in a study by Banuelos and Hanson [152], strawberry yields increased when Se-enriched seed meals produced from canola (*Brassica napus*) and mustard (*Sinapis alba*) plants were incorporated into soil as a fertilizer. The nutrient content of the fruit increased as a function of soil treatment and the Se-enriched amendment was effective at decreasing the emergence of summer-germinating and resident winter annual weeds [152]. Although, large scale trials are required, this work indicates that plants containing Se are likely to have an application in organic agriculture.

In addition to the great potential demonstrated in the formation and utilization of nanoparticles from phytoextracted biomass, the development of interesting nanostructured materials could expand the range of higher value applications, however, further green chemistry research is required to realize this potential.

5.4 Future advancements to improve phytoextraction and expand applications

Significant efforts are required to efficiently recover and recycle metals from contaminated biomass, and perhaps most importantly, to realize the economic potential of phytoextraction in the context of green chemistry [130]. Development of innovative technologies is required for the valorization of the process as a whole. At present, only plants containing Au, Cu, Se, Zn and Ti have been utilized directly in green chemistry. As such it is vital to further expand this range of elements and also applications, examples of suggested future applications can be seen in Figure 7 [142, 144, 151, 152, 155–161]. Nonetheless, work so far shows that synthesis of active nanoparticles by plants is feasible.

6 Conclusion

The gradual depletion of natural sources of metals, and the contamination of soils and water through the dispersion of those metals in the environment, is a growing problem. The use of life cycle assessments to better understand the flow of metals through the technosphere is a key tool in highlighting activities that lead to significant losses of metals. Life cycle assessment is not only focusing our attention on areas of concern, but identifying opportunities for further exploitation. The challenge then becomes one of applying a suitable technology to recover metal from newly defined resources, and it is in this context that we highlight the potential of phytoextraction. We propose that phytoextraction can be viewed as an important green method for remediation and metal acquisition. The creation of new hyperaccumulators through selective plant breeding or genetic engineering, and the development of novel routes to induce metal uptake will be critical research areas for phytoextraction in the future.

To date, the natural ability of plants to form metal nanoparticles has not been fully exploited. The use of plants to synthesize industrially and environmentally important nanoparticles is an area of green chemistry that has tremendous potential for the production of novel materials, catalysts and chemicals. Global research has conclusively demonstrated the promise that “phytoextracted” metals have in a limited number of applications to date. Further and innovative research is now required to enable this promising green technology to reach its full potential.

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References

[1] Hunt AJ, Farmer TJ, Clark JH. In *Element Recovery and Sustainability*, Hunt AJ, Ed., Royal Society of Chemistry: London, 2013, Vol. 22, pp. 1–28.
[2] Kalidindi SB, Jagirdar BR. *ChemSusChem* 2012, 5, 65–75.
[3] Crudwell FK, Moats MS, Ramachandran V, Robinson TG, Davenport WG. *Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals*, Elsevier: Oxford, 2011.
[4] Sheldon RA. *Chem. Ind.* 1997, 1, 12–15.
[5] Clark JH. *Green Chem.* 1999, 1, G1–G2.
[6] Graedel TE, Allwood J, Birat J-P, Buchert M, Hagelüken C, Reck BK, Sibley SF, Sonnemann G. *J. Ind. Ecol.* 2011, 15, 355–366.
[7] Reck BK, Graedel TE. *Science* 2012, 337, 690–695.
[8] Hudson-Edwards KA, Jamieson HE, Lottermoser BG. *Elements* 2011, 7, 375–380.
[9] Dodson JR, Hunt AJ, Parker HL, Yang Y, Clark JH. *Chem. Eng. Process.: Process. Intensif.* 2012, 51, 69–78.
[10] Pilon-Smits E. *Annu. Rev. Plant. Biol.* 2005, 56, 15–39.
[11] Wong MH. *Chemosphere* 2003, 50, 775–780.
[12] Mench M, Lepp N, Bert V, Schwitzguebel J-P, Gawronski SW, Schroder P, Vangronsveld J. *J. Soils Sed.* 2010, 10, 1039–1070.
[13] Lasat MM. *J. Environ. Qual.* 2002, 31, 109–120.
[14] Do Nascimento CWA, Xing B. *Sci. Agric.* 2006, 63, 299–311.
[15] Chaney R, Angle JS, Broadhurst CL, Peters CA, Tappero RV, Sparks DL. *J. Environ. Qual.* 2007, 36, 1429–1443.
[16] Moosavi SG, Seghatoleslami MJ. *Adv. Agri. Biol.* 2013, 1, 5–11.
[17] Anderson CWN. *J. Degrad. Mining Lands Manage.* 2013, 1, 51–56.
[18] Anderson CWN, Brooks RR, Chiarucci A, Lacoste CJ, Leblanc M, Robinson BH, Simcock R, Steward RB. *J. Geochem. Explor.* 1999, 67, 407–415.
[19] Reck BK, Muller DB, Rostkowski K, Graedel TE. *Environ. Sci. Technol.* 2008, 42, 3394–3400.
[20] Lottermoser BG. *Elements* 2011, 7, 405–410.
[21] Kumar V, Yaddav SK. *J. Chem. Technol. Biotechnol.* 2009, 84, 151–157.
[22] USGS Minerals Yearbook 2013, available at: http://minerals.usgs.gov/minerals/pubs/myb.html [Accessed 24 October, 2013].
[23] Wang T, Muller DB, Graedel TE. *Environ. Sci. Technol.* 2007, 41, 5120–5139.
[24] Gordon RB. *Resour. Conserv. Recy.* 2002, 36, 87–106.
[25] Norilsk, *Annual Report, OJSC MMC Norilsk Nickel*: Moscow, Russia, 2012.
[26] Mao JS, Dong J, Graedel TE. *Resour. Conserv. Recy.* 2008, 52, 1058–1064.
[27] Graedel TE, Van Beers D, Bertram M, Fuse K, Gordon RB, Gritsinin A, Harper EM, Kapur A, Klee RJ, Lifset R, Memon L, Spatari S. *J. Ind. Ecol.* 2005, 9, 67–90.
[28] Nassar NT. In *Elemental Recovery and Sustainability*, Hunt A, Ed., Royal Society of Chemistry: London, 2013, pp. 185–206.

[29] Kelly TD, Matos GR. U.S. Geological Survey, Historical statistics for mineral and material commodities in the U.S., Data series 140, http://minerals.usgs.gov/ds/2005/140/ [Accessed 22 September, 2013].
[30] USGS Minerals Yearbook 2009, available at: http://minerals.usgs.gov/minerals/pubs/myb.html [Accessed 22 September, 2013].
[31] Jolly JH. *Resour. Conserv. Recy.* 1993, 9, 1–30.
[32] Budarin VL, Shuttleworth PS, Dodson JR, Hunt AJ, Lanigan B, Marriot R, Milkowski KJ, Breeden SW, Fan J, Sin EHK, Clark JH. *Energy Environ. Sci.* 2011, 4, 471–479.
[33] Clark JH, Budarin VL, Deswarte FEI, Hardy JJE, Hunt AJ, Kerton RM, Luque R, Macquarrie DJ, Milkowski KJ, Rodriguez A, Samuel O, Tavener SJ, White RJ, Wilson AJ. *Green Chem.* 2006, 8, 853–860.
[34] Cunningham SD, Ow DW. *Plant Physiol.* 1996, 110, 715–719.
[35] Dodson JR, Hunt AJ, Budarin VL, Matharu AS, Clark JH. *RSC Adv.* 2011, 1, 523–530.
[36] Dodson JR, Cooper E, Hunt AJ, Matharu AS, Clark JH, Macquarrie DJ. *Green Chem.* 2013, 15, 1203–1210.
[37] Watanabe ME. *Environ. Sci. Technol.* 1997, 31, 182A–186A.
[38] Salt DE, Blaylock M, Kumar NPBA, Dushenkov V, Ensley BD, Chet I, Raskin I. *Biotechnol.* 1995, 13, 468–474.
[39] Butcher DJ. *Appl. Spectrosc. Rev.* 2009, 44, 123–139.
[40] Flathman PE, Lanza GR. *J. Soil. Contam.* 1998, 7, 415–432.
[41] Alkorta I, Hernández-Allica J, Becerril JM, Amezaga I, Albizu I, Garbisu C. *Rev. Environ. Sci. Biotechnol.* 2004, 3, 71–90.
[42] Pulford ID, Riddle-Black D, Stewart C. *Int. J. Phytorem.* 2002, 4, 59–72.
[43] Mcgrath SP, Sidoli CMD, Baker A, Reeves R. In *Integrated Soil and Sediment Research: A Basis for Proper Protection, Soil and Environment*, 1993, Vol. 1, pp. 673–676.
[44] Felix H. *Z. Pflanzenernähr. Bodenk.* 1997, 160, 525–529.
[45] Hammer D, Kayser A, Keller C. *Soil Use Manage.* 2003, 19, 187–192.
[46] Hammer D, Keller C. *Soil Use Manage.* 2003, 19, 144–149.
[47] Brown SL, Chaney RL, Angle JS, Baker A. *Environ. Sci. Technol.* 1995, 29, 1581–1585.
[48] Majid NM, Islam MM, Nap NE, Ghafoori M, Abdu A. *Acta Agr. Scan. B – S. P.* 2012, 62, 101–108.
[49] Knight B, Zhao FJ, Mcgrath SP, Shen ZG. *Plant Soil* 1997, 197, 71–78.
[50] Li Y-M, Chaney R, Brewer E, Angle JS, Nelkin J. *Environ. Sci. Technol.* 2003, 37, 1463–1468.
[51] Ibaraki T, Kuroyanagi N, Murakami M. *Soil Sci. Plant Nutr.* 2009, 55, 421–427.
[52] Kurihara H, Watanabe ME, Hayakawa T. *Jpn. J. Soil Sci. Plant Nutr.* 2005, 76, 27–34.
[53] Van Der Ent A, Baker A, Reeves R, Pollard AJ, Schat H. *Plant Soil.* 2012, 362, 319–334.
[54] Baker A, Walker PL. In *Heavy Metal Tolerance in Plants: Evolutionary Aspects*, Shaw AJ, Ed., CRC: Boca Raton, 1990.
[55] Ghosh M, Singh SP. *Appl. Ecol. Environ. Res.* 2005, 3, 1–18.
[56] Raskin I, Kumar PN, Dushenkov S, Salt DE. *Curr. Opin. Biotechnol.* 1994, 5, 285–290.
[57] Boularbah A, Schwartz C, Bitton G, Aboudrar W, Ouhammou A, Morel JL. *Chemosphere* 2006, 63, 811–817.
[58] Anderson CWN, Moreno F, Meech J. *Miner. Eng.* 2005, 18, 385–392.
[59] Lintern M, Anand R, Ryan C, Paterson D. *Nature Commun.* 2013, 4, 2274. DOI:10.1038/ncomms3614.
[60] Jaffré T, Brooks RR, Lee J, Reeves R. *Science* 1976, 193, 579–580.
[61] Anderson CWN. In *Element Recovery and Sustainability*, Hunt A, Ed., Royal Society of Chemistry: London, 2013, pp. 114–139.
[62] Baker AJM, Mcgrath SP, Sidoli CMD, Reeves RD. *Resour. Conserv. Recy.* 1994, 11, 41–49.
[63] Barman SC, Sahu RK, Bhargava SK, Chaterjee C. *Bull. Environ. Contam. Toxicol.* 2000, 64, 489–496.
[64] Haque N, Peralta-Videa JR, Jones GL, Gill TE, Gardea-Torresdey JL. *Environ. Pollut.* 2008, 153, 362–368.
[65] Robinson BH, Brooks RR, Howes AW, Kirkman JH, Gregg PEH. *J. Geochem. Explor.* 1997, 60, 115–126.
[66] Del Río-Celestino M, Font R, Moreno-Rojas R, De Haro-Bailón A. *Ind. Crop. Prod.* 2006, 24, 230–237.
[67] Robinson B, Chiarucci A, Brooks RR, Petit D, Kirkman JH, Gregg PEH, De Dominicis V. *J. Geochem. Explor.* 1997, 59, 75–86.
[68] Brooks RR, Radford CC. *Proc. R. Soc. London, Ser. B* 1978, 200, 217–224.
[69] Leblanc M, Petit D, Deram A, Robinson B, Brooks RR. *Econ. Geol.* 1999, 94, 109–114.
[70] Fischerová Z, Tlustoš P, Száková J, Šichorová K. *Environ. Pollut.* 2006, 144, 93–100.
[71] Reeves RD, Brooks RR, Macfarlane RM. *Am. J. Bot.* 1981, 68, 708–712.
[72] Reeves RD, Brooks RR. *Environ. Pollut. A* 1983, 31, 277–285.
[73] Brooks RR. *Plant Soil.* 1977, 48, 541–544.
[74] Liu X, Gao Y, Khan S, Duan G, Chen A, Ling L, Zhao L, Liu Z, Wu X. *J. Environ. Sci.* 2008, 20, 1469–1474.
[75] Reeves RD, Baker AJM, Bgrhidi A, Berazain R. *New Phytol.* 1996, 133, 217–224.
[76] Jaffré T, Brooks RR, Trow JM. *Plant Soil* 1979, 51, 157–161.
[77] Jaffré T. *Étude Écologique du Peuplement Végétal des sols Dérivés des Roches Ultrabasiques en Nouvelle Calédonie*, PhD thesis, (Services de publication de L'ORSTOM), 1980.
[78] Jaffré T, Schmid M. *C.R. Acad. Sci. D. Nat.* 1974, 278, 1727–1730.
[79] Jaffré T, Kersten WJ, Brooks RR, Reeves R. *Proc. R. Soc. London, Ser. B* 1979, 205, 385–394.
[80] Zhang X, Xia H, Li Z, Zhuang P, Gao B. *J. Hazard. Mater.* 2011, 189, 414–419.
[81] Brooks RR, Lee J, Reeves RD, Jaffré T. *J. Geochem. Explor.* 1977, 7, 49–57.
[82] Brooks RR, Wither ED. *J. Geochem. Explor.* 1977, 7, 295–300.
[83] Brooks RR, Wither ED, Zepernick B. *Plant Soil.* 1977, 47, 707–712.
[84] Jaffré T, Pillon Y, Thomine S, Merlot S. *Front. Plant Sci.* 2013, 4, 1–7.
[85] Krämer U. *Annu. Rev. Plant. Biol.* 2010, 61, 517–534.
[86] Li Y-M, Chaney R, Brewer E, Roseberg R, Angle JS, Baker A, Reeves R, Nelkin J. *Plant Soil* 2003, 249, 107–115.
[87] Oregon Invasive Species Council http://www.oregon.gov/OISC/Pages/most_dangerous.aspx, [Accessed 10 December, 2013].
[88] van der Ent A, Baker A, Van Balgooy MMJ, Tjoa A. *J. Geochem. Explor.* 2013, 128, 72–79.
[89] Chaney R, Broadhurst CL, Centofanti T. In *Trace elements in soils*, Hooda PS, Ed., Wiley: Chichester, 2010, pp. 311–325.
[90] Greger M, Landberg T. *Int. J. Phytorem.* 1999, 1, 115–123.

[91] Wilson-Corral V, Anderson CWN, Rodriguez-Lopez M. *J. Environ. Manage.* 2012, 111, 249–257.
[92] Tandy S, Schulin R, Nowack B. *Environ. Sci. Technol.* 2006, 40, 2753–2758.
[93] Do Nascimento CWA, Amarasiriwardena D, Xing B. *Environ. Pollut.* 2006, 140, 114–123.
[94] Blaylock MJ, Salt DE, Dushenkov S, Zakharova O, Gussman C, Kapulnik Y, Ensley BD, Raskin I. *Environ. Sci. Technol.* 1997, 31, 860–865.
[95] Quartacci MF, Baker AJM, Navari-Izzo F. *Chemosphere* 2005, 59, 1249–1255.
[96] Anderson CWN, Brooks RR, Steward RB, Simcock R. *Nature* 1998, 395, 553–554.
[97] Anderson CWN, Bhatti SM, Gardea-Torresdey J, Parsons J. *ACS Sustain. Chem. Eng.* 2013, 1, 640–648.
[98] Kayser A, Wenger K, Keller A, Attinger W, Felix H, Gupta SK, Schulin R. *Environ. Sci. Technol.* 2000, 34, 1778–1783.
[99] Huang JW, Chen J, Berti WR, Cunningham SD. *Environ. Sci. Technol.* 1997, 31, 800–805.
[100] Duo L-A, Gao Y-B, Zhao S-L. *J. Intergr. Plant Biol.* 2005, 47, 1047–1054.
[101] Chiu KK, Ye ZH, Wong MH. *Chemosphere* 2005, 60, 1365–1375.
[102] Ullmann A, Brauner N, Vazana S, Katz Z, Goikhman R, Seemann B, Marom H, Gozin M. *J. Hazard. Mater.* 2013, 260, 676–688.
[103] Batty LC, Dolan C. *Crit. Rev. Env. Sci. Technol.* 2013, 43, 217–259.
[104] Evangelou MWH, Ebel M, Scheffer A. *Chemosphere* 2007, 68, 989–1003.
[105] Shahid M, Austruy A, Echevarria G, Arshad M, Sanaullah M, Aslam M, Nadeem M, Nasim W, Dumat C. *Soil Sediment Contam.* 2014, 23, 389–416.
[106] Meers E, Tack FMG, Van Slycken S, Ruttens A, Du Lating G, Van Gronsveld J, Verloo MG. *Int. J. Phytorem.* 2008, 10, 390–414.
[107] Agnello AC, Huguenot D, Van Hullebusch ED, Esposito G. *Crit. Rev. Env. Sci. Technol.* 2013. DOI:10.1080/10643389.2013.829764.
[108] Becher M, Talke IN, Krall L, Krämer U, *Plant J.* 2004, 37, 251–268.
[109] Weber M, Harada E, Vess C, Roepenack-Lahaye EV, Clemens S. *Plant J.* 2004, 37, 269–281.
[110] Mendoza-Cózatl DG, Jobe TO, Hauser F, Schroeder JI. *Curr. Opin. Plant Biol.* 2011, 14, 554–562.
[111] Rascio N, Navari-Izzo F. *Plant Sci.* 2011, 180, 169–181.
[112] Hanikenne M, Talke IN, Haydon MJ, Lanz C, Nolte A, Motte P, Kroymann J, Weigel D, Krämer U. *Nature* 2008, 453, 391–395.
[113] Dhankher OP, Li Y, Rosen BP, Shi J, Salt D, Senecoff JF, Sashti NA, Meagher RB. *Nat. Biotechnol.* 2002, 20, 1140–1145.
[114] Bizily SP, Rugh CL, Meagher RB. *Nat. Biotechnol.* 2000, 18, 213–217.
[115] Adams JP, Adeli A, Hsu CY, Harkess RL, Page GP, Schultz EB, Yuceer C. *J. Exp. Biol.* 2011, 62, 3737–3752.
[116] Bittsánszky A, Kömives T, Gullner G, Gyulai G, Kiss J, Heszky L. *Environ. Int.* 2005, 31, 251–254.
[117] Lyyra S, Meagher RB, Kim T, Heaton A, Montello P, Balish RS, Merkle SA. *Plant Biotechnol. J.* 2007, 5, 254–262.
[118] Maestri E, Marmiroli N. *Int. J. Phytorem.* 2011, 13, 264–279.
[119] Veiga MM, Nunes D, Klien B, Shandro JA, Velasques PC, Sousa RN. *J. Cleaner Prod.* 2009, 17, 1373–1381.
[120] Krisnayanti BD, Anderson CWN, Utomo WH, Feng X, Handayanto E, Mudarisna N, Ikramb H, Khususiahb. *J. Environ. Manage.* 2012, 14, 2598–2607.
[121] Singh OV, Labana S, Pandey G, Budhiraja R, Jain RK. *Appl. Microbiol. Biotechnol.* 2003, 61, 405–412.
[122] Shah K, Nongkynrih JM. *Biol. Plant.* 2007, 51, 618–634.
[123] Bradshaw A. *Ecol. Eng.* 1997, 8, 255–269.
[124] Cunningham SD, Berti WR. *In Vitro Cell. Dev. Biol. Anim.* 1993, 29, 207–212.
[125] Schnoor JL, Licht LA, Mccutcheon SC, Wolfe NL, Carreira LH. *Environ. Sci. Technol.* 1995, 29, 318–323.
[126] Macek T, Macková M, Káš J. *Biotechnol. Adv.* 2000, 18, 23–34.
[127] Robinson B, Brooks RR, Gregg PEH, Kirkman JH. *Geoderma* 1999, 87, 293–304.
[128] Harris AT, Naidoo K, Nokes J, Walker T, Orton F. *J. Cleaner Prod.* 2009, 17, 194–200.
[129] Jambhulkar HP, Juwarkar AA. *Ecotoxicol. Environ. Saf.* 2009, 72, 1122–1128.
[130] Losfeld G, Vidal De Le Blache P, Escande V, Grison C. *Green Chem. Lett. Rev.* 2012, 5, 451–456.
[131] Harris AT, Bali R. *J. Nanopart. Res.* 2008, 10, 691–695.
[132] Astruc D, Lu F, Ruiz Aranzaes J. *Angew. Chem. Int. Ed.* 2005, 44, 7852–7872.
[133] The Royal Society and The Royal Academy of Engineering, *Nanoscience and Nanotechnology: Opportunities and Uncertainties* (The Royal Society, 2004) http://www.nanotec.org.uk, [Accessed 13 December, 2013].
[134] Académie des Sciences, Académie des Technologies, *Nanosciences - Nanotechnologies,* Science and Technology Report No. 18 (French Academy of Sciences, 2004); summary of recommendations (in English) http://www.developpement-durable.gouv.fr/IMG/pdf/CPP_Nanotech-nologiesNanoparticles.pdf, [Accessed 13 December, 2013].
[135] Nanoscalse Science Engineering and Technology Subcommittee, *The National Nanotechnology Initiative: Nanotechnology 101* (US National Science and Technology Council, 2004) http://www.nano.gov/nanotech-101#content, [Accessed 13 December, 2013].
[136] Auffan M, Rose J, Bottero J-Y, Lowry GV, Jolivet J-P, Wiesner MR. *Nature Nanotech.* 2009, 4, 634–641.
[137] White RJ, Luque R, Budarin VL, Clark JH, Macquarrie DJ. *Chem. Soc. Rev.* 2009, 38, 481–494.
[138] Ren X, Meng X, Tang F, *Sens. Actuators, B* 2005, 110, 358–363.
[139] Losfeld G, Escande V, Vidal De Le Blache P, L'huilluer L, Grison C. *Catal. Today* 2012, 189, 111–116.
[140] Iravani S. *Green Chem.* 2011, 13, 2638–2650.
[141] Goesmann H, Feldmann C. *Angew. Chem. Int. Ed.* 2010, 49, 1362–1395.
[142] Sharma NC, Sahi SV, Nath S, Parsons J, Gardea-Torresdey J, Pal T. *Environ. Sci. Technol.* 2007, 41, 5137–5142.
[143] Kandiel TA, Feldhoff A, Robben L, Dillert R, Bahnemann DW. *Chem. Mater.* 2012, 22, 2050–2060.
[144] Mahmood T, Hussain ST, Malik SA. *African J. Biotech.* 2010, 9, 2381–2391.
[145] Dodson J, Parker H. In *Element Recovery and Sustainability*, Hunt A, Ed., Royal Society of Chemistry: London, 2013, pp. 220–258.
[146] Dykman L, Khlebtsov N. *Chem. Soc. Rev.* 2012, 41, 2256–2282.

[147] Cobley CM, Chen J, Cho EC, Wang LV, Xia Y. *Chem. Soc. Rev.* 2011, 40, 44–56.
[148] Giljohann DA, Seferos DS, Daniel WL, Massich MD, Patel PC, Mirkin CA. *Angew. Chem. Int. Ed.* 2010, 49, 3280–3294.
[149] Dreaden EC, Alkilany AM, Huang X, Murphy CJ, El-Sayed M. *Chem. Soc. Rev.* 2012, 41, 2740–2779.
[150] Boisselier E, Astruc D. *Chem. Soc. Rev.* 2009, 38, 1759–1782.
[151] Liu W-J, Tian K, Jiang H, Zhang X-S, Ding H-S, Yu H-Q. *Environ. Sci. Technol.* 2012, 46, 7849–7856.
[152] Banuelos GS, Hanson BD. *HortScience* 2010, 45, 1567–1572.
[153] Zhu Y-G, Pilon-Smits EaH, Zhao F-J, Williams PN, Meharg AA. *Trends Plant Sci.* 2009, 14, 436–442.
[154] Banuelos GS. *Environ. Pollut.* 2005, 144, 19–23.
[155] Kavlak G, Graedel TE. *Resour. Conserv. Recy.* 2013, 73, 17–22.
[156] Dou L, Chang W-H, Gao J, Chen C-C, You J, Yang Y. *Adv. Mater.* 2013, 25, 825–831.
[157] Battin EE, Brumaghim JL. *Cell Biochem. Biophys.* 2009, 55, 1–23.
[158] Lu L-M, Zhang X-B, Shen G-L, Yu R-Q. *Anal. Chim. Acta* 2012, 715, 99–104.
[159] Luechinger NA, Athanassiou EK, Stark WJ. *Nanotechnology* 2008, 19, 1–6.
[160] Hayashi T, Tanaka K, Haruta M. *J. Catal.* 1998, 178, 566–575.
[161] Grisel R, Weststrate K-J, Gluhoi A, Nieuwenhuys BE. *Gold Bulletin* 2002, 35, 39–45.

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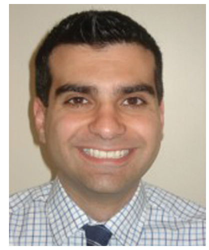

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