Global Distribution and Ecology of Hyperaccumulator Plants

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Abstract

A large body of analytical data is available on the inorganic composition of many thousands of plant species, for which typical concentration ranges have been tabulated for major, minor, and trace elements. These elements include those that have been shown essential for plant growth, as well as others that lack this status, at least universally. Metalliferous soils, having abnormally high concentrations of some of the elements that are generally present only at minor (e.g. 200–2000 μg g^{-1}) or trace (e.g. 0.1–200 μg g^{-1}) levels, vary widely in their effects on plants and have attracted increasing attention during the last 50 years. The effects depend on the species, the relevant elements, and soil characteristics that influence the availability of metals to plants. Some of these soils are toxic to all or most higher plants. Others have hosted the development of specialized plant communities consisting of a restricted and locally characteristic range of metal-tolerant species. These plants often show a slightly elevated concentration of the elements with which the soil is enriched, but in places a species exhibits extreme accumulation of one or more of these elements, to a concentration level that may be hundreds or even thousands of times greater than that usually found in plants on the most common soils. These plants, now widely referred to as hyperaccumulators, are a remarkable resource for many types of fundamental scientific investigation (plant systematics, ecophysiology, biochemistry, genetics, and molecular biology) and for applications such as phytoremediation and agromining, and are discussed in detail below.

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1 Introduction

It has been known since the 1850s and 1860s that certain plant species then found on the zinc (Zn)-rich ‘calamine’ soils near Aachen in Germany accumulated Zn to very high concentrations. Although the first record referred to *Viola calaminaria* (Violaceae), a later report presented data showing that *Thlaspi alpestre* var. *calaminare,* now classified as *Noccaea caerulescens* (Brassicaceae), contained at least 1% Zn in the dry leaf tissue, or 10% in the inorganic ash (Sachs 1865). Plants of the genus *Noccaea* (earlier included in *Thlaspi sensu lato*) are discussed in more detail below. During the last 100 years, unusual accumulation of other metals and metalloids has been found: selenium (Se) in the 1930s; nickel (Ni) in the 1940s; cobalt (Co), copper (Cu), and arsenic (As) in the 1960s; and cadmium (Cd) and manganese (Mn) in the 1970s.

2 Hyperaccumulation

Normal concentration ranges in plants have been tabulated for major, minor, and trace elements in many reviews (e.g. Reeves and Baker 2000). The term ‘hyperaccumulation,’ describing a highly abnormal level of metal accumulation, was first applied by Jaffré et al. (1976) in the title of their paper on Ni concentrations in the New Caledonian tree *Sebertia acuminata* (Sapotaceae), now classified as *Pycnandra acuminata*. In discussing Ni concentrations in species of *Homalium* (Salicaceae) and *Hybanthus* (Violaceae) from various parts of the world, Brooks et al. (1977a) used the term to indicate a defined concentration threshold (>1000 μg g^{-1}) for Ni. A similar concept was used earlier by Jaffré and Schmid (1974), who referred to certain Ni-rich plants from the ultramafic soils of New Caledonia as ‘hypernickelophores,’ i.e. ‘extreme nickel-bearers.’

The choice of the 1000 μg g^{-1} criterion was not entirely arbitrary. In many reports on Ni-rich soils, plant Ni concentrations are generally 5–100 μg g^{-1}; levels of 100–1000 μg g^{-1} are quite rare; the local cases of accumulation to >1000 μg g^{-1} seem to represent a distinct form of plant response, implying some characteristic and unusual physiological behaviour. Greater precision in the definition of hyperaccumulation was provided by Reeves (1992) for Ni: *“a hyperaccumulator of Ni is a plant in which a Ni concentration of at least 1000 mg/kg has been recorded in the dry matter of any above-ground tissue in at least one specimen growing in its natural habitat.*” The criteria defining hyperaccumulation should therefore not be based on analyses of whole plants or subterranean plant parts, largely because of the difficulty of ensuring that the samples are free of soil contamination, but also because plants that immobilize metals in the root system, and fail to translocate them further (Baker 1981), are of less interest for many purposes than those that actively accumulate metals into all tissues.

Definitions of hyperaccumulation have been extended to elements other than Ni. Malaisse et al. (1978) used the 1000 μg g^{-1} criterion for Cu accumulation, and Brooks et al. (1980) applied this to Co. Reeves and Brooks (1983b) used the same criterion in discussing lead, but for Mn and Zn, which are normally present at higher and more widely varying concentrations (~20–400 μg g^{-1}), a 10,000 μg g^{-1} threshold was suggested by Baker and Brooks (1989), following use of the term ‘hypermanganèsophore’ for plants having this level of Mn accumulation (Jaffré 1980).

Extensive recent discussions of appropriate criteria for defining hyperaccumulation of many elements are those of Baker et al. (2000), Baker and Whiting (2002) and van der Ent et al. (2013) who summarized the history of the development of this topic. These papers also pay attention to the limitations of hydroponic experiments in relation to hyperaccumulation, because these experiments have often involved the use of unrealistic concentrations of free metal ions that are not relevant to the continuing life cycle of naturally occurring metallophyte populations living on metalliferous soils.

3 Ecology and Conservational Status of Hyperaccumulator Plants

The soils produced from the weathering of surficial ore deposits or naturally enriched metalliferous country rocks (e.g. ultramafics, Cu-Co mineralization, calamine deposits) can be regarded as primary habitats for most hyperaccumulator plants. In certain cases, as in some of the ultramafic terraines of Cuba and New Caledonia, such soils are believed to have been continuously available for plant life and evolution for millions of years (Reeves et al. 1996, 1999). Other naturally occurring metalliferous soils are much younger, having been subjected to more recent geological processes such as erosion and re-deposition, hydrothermal alteration, or glaciation. Secondary habitats (on the scale of decades to a few thousand years) have resulted from the exploitation of mineral deposits via metalliferous mining and ore processing activities. A tertiary category of distribution results from the superficial deposition of dusts and particles derived from smelting operations and the beneficiation of processed ores where effluents are discharged into river systems leading to metal enrichment of alluvial floodplains (Baker et al. 2010).

Present-day plant species that show metal tolerance through occurrence on metalliferous soils may therefore have experienced any of this wide variety of soil histories. In relation to species that appear to be endemic to metalliferous soils, there has been extensive discussion of the concepts of palaeo-endemism and neo-endemism (Stebbins 1942; Kruckeberg 1954; Antonovics et al. 1971; Brooks 1987, pp. 70–71). Palaeoendemics are supposed to be relics of formerly widespread species that have survived in the metalliferous environment, restricted by competitive pressures and often having no or few closely related surviving species. Neo-endemic metallophytes are species that have evolved from a parent in the metalliferous environment, leading to morphological characteristics now recognized as distinctive. The concept as applied generally to metallophytes can also be used in discussion of the particular case of hyperaccumulator species and their putative origins. Some Ni hyperaccumulators, for example, in genera consisting of only one or two species on ancient soils and without close relatives, may be palaeo-endemics. Examples include *Shafera platyphylla* (Asteraceae) and *Phyllomelia coronata* (Rubiaceae) from Cuba. These phylogenetically isolated hyperaccumulators contrast with the situation in some genera where actively evolving speciation appears to be continuing, as shown by the large numbers of Ni hyperaccumulating endemics present in genera such as *Alyssum* (Brassicaceae) in Mediterranean Europe, Turkey, and nearby parts of Asia—Fig. 1; *Buxus* (Buxaceae) and *Leucocroton* (Euphorbiaceae) in Cuba; and *Phyllanthus* (Phyllanthaceae) in several tropical parts of the world.

Mineral wastes have enabled locally endemic species that are both hypertolerant and hyperaccumulating to extend their distributions regionally, such that the current distributions of some hyperaccumulator plants have extended well beyond primary habitats. Additionally, some species are known from both non-metalliferous and metalliferous locations, exhibiting hyperaccumulation solely from the latter. This situation, described as 'facultative hyperaccumulation' has been discussed in detail by Pollard et al. (2014). Further, some species have been reported to show extreme accumulation of some elements (e.g. Zn, Mn, Se) from normal soils or those with only modest elevations of the element concerned. Examples include: *Noccaea caerulescens* (Brassicaceae) that hyperaccumulates Zn from both metalliferous and non-metalliferous soils in France and elsewhere in Europe (Reeves et al. 2001); *Gossia* (formerly *Austromyrtus*) *bidwillii* (Myrtaceae)

Fig. 1 The field spot test based on dimethylglyoxime applied to the Ni hyperaccumulator *Alyssum murale* (Brassicaceae) from Albania

from eastern Australia (Bidwell et al. 2002; Fernando et al. 2009), and *Alyxia rubricaulis* (Apocynaceae) from New Caledonia (Jaffré 1980) that hyperaccumulates Mn from soils having only a slightly elevated Mn content; and species of *Astragalus* (Fabaceae) in the USA (Rosenfeld and Beath 1964) that hyperaccumulate selenium from soils in which the elevated Se content is commonly $<50\ \mu g\ g^{-1}$.

In temperate regions, the plant assemblages on metalliferous soils generally consist of a limited range of absolute and pseudo-metallophytes (Baker 1987) that may or may not include hyperaccumulators. On ultramafic soils, in particular in Mediterranean Europe, there can frequently exist a nearly monospecific community of a Ni hyperaccumulator, e.g. *Alyssum* spp. in Greece, Turkey, and Albania. By contrast, in the tropics ultramafic soils regularly show a high density of woody species where hyperaccumulators and non-hyperaccumulators may grow side by side. Often the most ancient and undisturbed metalliferous environments support the richest assemblages of hyperaccumulator plants (e.g. Reeves et al. 1996, 1999).

In spite of the rapidly increasing number of hyperaccumulator plants being discovered (especially for Ni), the overall rarity of this resource must be stressed. Furthermore, anthropogenic and environmental factors threaten the habitats of many hyperaccumulator plants. These include: ongoing mineral exploration and mining activities, reworking of ancient mine spoils, land reclamation and improvement for agricultural production, urbanization and development of brownfield sites, natural fire events, and probably climate change (Whiting et al. 2004; Baker et al. 2010; Wulff et al. 2013). Urgent conservation and management steps are clearly needed in areas under threat, in order to ensure the persistence of the valuable phytotechnological resource. Appropriate options are the maintenance of living materials in botanical gardens and seed in germplasm banks, and regeneration in situ using 'seed orchards' on mining lands. Exploitation of the hyperaccumulator resource base for agromining must be considered with due caution and with appropriate management practices in place. An unfortunate incident has been reported in southwestern Oregon, where poor crop management led to the extension of the distribution of *A. murale* well outside of the operational area, to the extent that it is now regarded as a noxious weed in Oregon and future use has been banned (Strawn 2013). Invasions such as this may also affect the status of other local endemics native to the area that have been selected for agromining.

4 Instances of Hyperaccumulation

The following discussion outlines instances of hyperaccumulation of selected trace elements (Ni, Zn, Cd, Pb, Co, Cr, Cu, Mn, Se, As and Tl) for which a substantial body of reliable plant analysis data exists. Further exploration of various types of metalliferous environments, both natural and man-modified, will certainly uncover more examples. The exact enumeration of metal hyperaccumulator species is made difficult by the lack of recent and complete Floras for many tropical regions, in particular. The exact identification of some specimens of interest is still in doubt. In addition, since the first hyperaccumulator species were identified, numerous name changes have occurred, some species have been grouped into synonymy, whereas others have been split into several taxa (species, subspecies and varieties). Some of the earlier information was published in periodicals that are difficult to access, and much useful detail has been omitted because of the space limitations of most journals. All of these difficulties have justified the initiative to create a Global Hyperaccumulator Database (www.hyperaccumulators.org), an ongoing project to encompass as much of the knowledge as possible on identified hyperaccumulator species, including synonymies and other taxonomic changes.

4.1 Nickel

Unprecedented Ni concentrations (up to about 10,000 μg g^{-1} or 1%) were discovered in the Italian serpentine plant *Alyssum bertolonii* (Brassicaceae) (Minguzzi and Vergnano 1948). In the 1960s, two additional Ni-accumulating *Alyssum* species—*A. murale* from Armenia (Doksopulo 1961) and *A. serpyllifolium* ssp. *lusitanicum* from Portugal (Menezes de Sequeira 1969)—were reported to behave similarly. These observations were followed by studies in Zimbabwe (Wild 1970) and two independent discoveries of high Ni concentrations (3000–9800 μg g^{-1}) in *Hybanthus floribundus* from Western Australia (Severne and Brooks 1972; Cole 1973).

Beginning in 1974, concerted attempts were made to discover the extent of Ni hyperaccumulation, both geographically and in terms of distribution in the plant kingdom. Detailed studies of the flora of ultramafic soils were carried out in New Caledonia (Jaffré and Schmid 1974; Jaffré et al. 1976, 1979a, b; Jaffré 1980). Particularly notable was the discovery that the latex of the New Caledonian tree *Pycnandra* (formerly *Sebertia*) *acuminata* contained about 10% Ni, yielding a dried solid with 20–25% Ni (Jaffré et al. 1976), in which citrate was a major organic constituent (Lee et al. 1977)—Fig. 2.

During the next 25 years, R.R. Brooks, R.D. Reeves, A.J.M. Baker, and co-workers in many other parts of the world collected and analyzed plant material from ultramafic areas in the search for further examples of Ni hyperaccumulation. Extensive use was made initially of leaf fragments from herbarium collections, but later this gave way to field studies. Brooks et al. (1977a) identified several species of *Homalium* and *Hybanthus* in New Caledonia as hyperaccumulators. A comprehensive survey of nearly all of the 170 known species of *Alyssum* (Brooks and Radford 1978; Brooks et al. 1979) established the existence of 48 Ni hyperaccumulators, all in one section (Odontarrhena) of the genus, distributed from Portugal across Mediterranean Europe to Turkey, Armenia, Iraq, Iran, and Russia. Most are ultramafic-endemic species, and many have a very restricted distribution. Several additions to the list of *Alyssum* Ni hyperaccumulators have been made subsequently.

Further work by various groups has focused on other genera of the Mediterranean region, on species of ultramafic outcrops in the European Alps, southern Africa, Newfoundland, and the Pacific Northwest of the United States, and on plants of tropical ultramafic soils of Brazil, Cuba, and other Caribbean islands, Queensland, Costa Rica, Sri Lanka, and Southeast Asia (especially certain islands of Indonesia and the Philippines). Hyperaccumulators discovered from temperate-

Fig. 2 The Ni hyperaccumulator *Pycnandra acuminata* (Sapotaceae) from New Caledonia has a peculiar blue-green latex with up to 25% Ni

Fig. 3 The Ni hyperaccumulator *Bornmuellera tymphaea* (Brassicaceae) from Greece can accumulate up to 3% foliar Ni

zone areas include *Leptoplax* (formerly *Peltaria*) *emarginata* from Greece (Reeves et al. 1980), species of *Bornmuellera* —Fig. 3 and *Cochlearia* (*Pseudosempervivum*) from Turkey and the Balkans (Reeves et al. 1983a; Reeves and Adıgüzel 2008), *Streptanthus polygaloides* from California (Reeves et al. 1981), and species of *Thlaspi* (*Noccaea*) from Europe (Reeves and Brooks 1983a), Turkey, and Japan (Reeves 1988; Reeves and Adıgüzel 2008), and California (Reeves et al. 1983b). Discoveries from tropical areas include several species from Palawan (Baker

Fig. 4 The Ni hyperaccumulator *Psychotria gabriellae* (Rubiaceae) from New Caledonia can accumulate in excess of 4% Ni

et al. 1992) and other parts of Southeast Asia (Wither and Brooks 1977), *Stackhousia tryonii* from Queensland (Batianoff et al. 1990), and numerous species from Brazil (Reeves et al. 2007).

The ultramafic soils of Cuba host the largest number of Ni hyperaccumulators reported from any one country. Following initial observations by Berazaín (1981), a survey of much of the Caribbean ultramafic flora revealed 128 such species in Cuba, as well as *Phyllanthus nummularioides* from the Dominican Republic (Reeves et al. 1996, 1999). *Psychotria grandis* is a Ni hyperaccumulator where it occurs on ultramafic soils in Puerto Rico (Reeves 2003; Campbell et al. 2013; McAlister et al. 2015). Other major sources of Ni hyperaccumulator plants, with more than 50 species each, are New Caledonia (see Fig. 4 for an example) and Turkey. Substantial additions to the list are being made from ongoing work in New Caledonia (Jaffré et al. 2013), Brazil, Indonesia (Halmahera and some of the smaller islands), Sabah (Malaysia) (van der Ent et al. 2015), and the Philippines (Fernando et al. 2013).

The most recent information brings the worldwide total of known Ni hyperaccumulator plant species to more than 450. Developments can be followed through earlier summaries, some of which deal with hyperaccumulators of other elements (Brooks 1987, 1998; Baker and Brooks 1989; Reeves et al. 1996, 1999; Reeves and Baker 2000; Reeves 2003, 2005); more recent results can be found in reports on work in Brazil by Reeves et al. (2007), and in Turkey by Reeves and Adıgüzel (2004, 2008). Ongoing investigations in Sabah (Malaysia) and New Caledonia continue to reveal numerous hyperaccumulator plants new to science (van der Ent et al. unpublished data).

Most Ni hyperaccumulators belong to two groups, geographically: (1) the Mediterranean region, extending from Portugal through Italy and the Balkans to Turkey and adjacent countries; and (2) tropical and subtropical areas worldwide, particularly Cuba, New Caledonia, and various islands of Indonesia and the Philippines. The plant family most strongly represented in the first group is Brassicaceae, whereas in tropical areas there is strong representation from Euphorbiaceae, Phyllanthaceae, Salicaceae, Buxaceae, and Rubiaceae. Within Violaceae, species of *Hybanthus* (Severne and Brooks 1972; Brooks et al. 1974; Jaffré 1980) and *Rinorea* (Brooks and Wither 1977; Brooks et al. 1977b; Proctor et al. 1994) are notable as having potentially suitable biomass for agromining purposes. Hyperaccumulators in the Asteraceae occur in South Africa (*Berkheya* and *Senecio*; Morrey et al. 1989, 1992), in the

Mediterranean-Turkey region (*Centaurea*; Reeves and Adıgüzel 2004), and in the neotropics (e.g. *Pentacalia* and *Senecio* in Cuba, Reeves et al. 1999; and in species in several genera from Brazil, Reeves et al. 2007). The Ni hyperaccumulator plants reported to date belong to about 40 different families, distributed widely throughout the plant kingdom; this property is therefore presumed to have evolved independently many times.

The relatively large number of Ni hyperaccumulators discovered (compared with those of other elements) may be partly the result of the concerted attention to analytical work on ultramafic floras and partly to the ability to detect high Ni concentrations (>1000 μg g^{-1}) in leaf tissue by a simple test with dimethylglyoxime. However, among various types of metalliferous soils, the Ni-enriched ultramafics are the most widespread on a global scale, and in places continuous ultramafic areas of tens or even hundreds of km^2 can be found (e.g. New Caledonia, Cuba and Turkey). Where such areas have been continuously available for plant colonization for millions of years, as appears to be the case in New Caledonia and eastern Cuba, a long-term opportunity has existed for the evolution of a characteristic flora with numerous endemic species, including some that have developed Ni accumulation as a particular response to growth on high-Ni soils.

Most of the known Ni hyperaccumulator species are endemic to ultramafic rocks, but some occur on a wider variety of soils and exhibit facultative hyperaccumulation, i.e. high Ni concentrations are found only in those specimens from Ni-rich soils. A tabulation of facultative hyperaccumulators, covering Ni and other elements, has been given by Pollard et al. (2014). In a few cases, ultramafic-endemic species may show a wide variation in Ni uptake, apparently being sensitive to parameters other than total soil Ni concentration, such as soil pH; this 'erratic' Ni hyperaccumulation occurs, for example, in the Queensland ultramafic endemic *Pimelea leptospermoides* (Reeves et al. 2015). It is certain that many further examples of Ni hyperaccumulation remain to be discovered. These will include species not yet discovered or described, and known species that have never been analyzed. Further studies of plants growing on ultramafic areas in several islands of the Philippines and Indonesia, in Central America, mainland Asia, and possibly West Africa, are particularly likely to be fruitful.

When the focus is specifically on agromining potential, the interest logically moves towards those species that contain consistently >1% Ni in their leaves (and ideally >1% in the total harvestable biomass). This property needs to be considered in conjunction with the rate of biomass production, and a number of other agronomic features as reviewed by Nkrumah et al. (2016). The observation that the Californian *Streptanthus polygaloides* (Brassicaceae) could accumulate Ni to 1.5% of the dry plant matter (Reeves et al. 1981) stimulated a study by Nicks and Chambers (1995, 1998) of the use of this plant for phytomining. This included investigations of various fertilization regimes and the optimization of harvest time. They estimated that a crop of nearly 5 t ha^{-1} could be obtained with unfertilized plants in a small-scale trial in the native environment, and predicted that fertilization could double that yield. Work elsewhere has been carried out with species capable of producing a larger biomass. The discovery of Ni hyperaccumulation by the South African *Berkheya coddii* (Morrey et al. 1989, 1992; Howes 1991) has been followed by extensive work on its cultivation and extraction of the accumulated Ni (Brooks and Robinson 1998; Robinson et al. 1997a). Yields in excess of 20 t ha^{-1} were calculated, again by extrapolation from studies involving small plots.

Several of the *Alyssum* hyperaccumulators have attracted attention for their phytoextraction potential. Although some work has been done on *A. bertolonii* (Robinson et al. 1997b), more investigations have centred on species that have higher biomass such as *A. corsicum* and *A. murale*, in particular (Li et al. 2003; Bani et al. 2015a, b) Other species of the Brassicaceae in the Mediterranean region, such as *Leptoplax* *emarginata* and *Bornmuellera tymphaea* (both Brassicaceae), have also been studied (Chardot et al. 2005). These authors concluded that *L. emarginata* compared favourably with *A. murale* and *Noccaea caerulescens* in its phytoextraction performance.

About 70 tropical hyperaccumulator taxa with >1% Ni have been listed by Reeves (2003). These include the facultative hyperaccumulator *Rinorea bengalensis* (Violaceae) of Southeast Asia, a large number of Cuban species in the Buxaceae, Phyllanthaceae and Rubiaceae, and several New Caledonian species. Many of these are shrubs or small trees, probably with good rates of biomass production, but in many cases no further information is available about cultivation requirements and reproduction. Some of these species are rare, and in most cases agronomic studies are lacking or are in early stages.

4.2 Zinc, Lead, and Cadmium

Since the early discovery of Zn accumulation by certain *Thlaspi* species (noted above), further work, particularly on *Thlaspi* from German and Belgian calamine soils and from British mine wastes, has been reported frequently, as discussed with detailed references by Baker et al. (1994), Reeves and Baker (2000), and Reeves et al. (2001). This species, often referred to as *Thlaspi calaminare* or *T. alpestre* in earlier work, and later as *T. caerulescens*, is now classified as *Noccaea caerulescens* after a taxonomic revision by Meyer (1973) and DNA analysis (Koch and Mummenhoff 2001; Al-Shehbaz 2014).

Following the observation of Rascio (1977) that *T. rotundifolium* ssp. *cepaeifolium* from Zn-polluted soils near the border of Italy and Austria was also a hyperaccumulator of Zn, surveys of the genus *Thlaspi sensu lato* (Reeves and Brooks 1983a, b; Reeves 1988) revealed that many species of this genus are hyperaccumulators of Ni from ultramafic soils and often have Zn levels above 1000 μg g^{-1}, even from soils of background Zn content. Reeves and Baker (1984) showed that the ability of the Austrian species *T. goesingense* to accumulate Ni and Zn was an innate or 'constitutional' property, not dependent on the geochemistry of the area from which the seed originated. Baker et al. (1994) showed that *T. caerulescens* grown in amended nutrient solutions had the ability to accumulate to high concentrations a wide variety of elements (Zn, Cd, Co, Mn and Ni throughout the plant; aluminium, chromium, Cu, iron, and lead largely into the root system).

There are several other examples of accumulation of Zn to the level of 10,000 μg g^{-1} set as the criterion for Zn hyperaccumulation by Baker and Brooks (1989), but this was lowered to 3,000 μg g^{-1} by Broadley et al. (2007), Krämer (2010) and van der Ent et al. (2013). The most notable example is probably *Arabidopsis* (formerly *Cardaminopsis*) *halleri* (Brassicaceae) (Ernst 1968). Other examples, mainly from the Zn-rich soils around mine sites or from the vicinity of smelters, are listed elsewhere (e.g. Reeves and Baker 2000).

Lead is usually present in foliar concentrations below <10 μg g^{-1}. Even where concentrations of 1–10 μg g^{-1} are measured in aboveground plant parts, it is likely that much of this comes from various forms of environmental contamination. Plant root systems restrict severely the uptake of this element and significant translocation to the upper parts is uncommon in plants in natural environments. There have been several reports of very high lead concentrations in plants from areas of Zn-Pb mineralization, or from mine or smelter wastes; notably, these have not generally been subjected to rigorous scrutiny in relation to washing procedures and contamination possibilities. Increased lead uptake can be achieved in hydroponic experiments or by various treatments of soil with complexing agents (Raskin and Ensley 2000). However, such soil treatments designed to mobilize relatively insoluble elements such as lead into harvestable plants, as promoted by several groups, are now regarded as being both economically and environmentally unfavourable.

Elevated levels of Cd (10–200 μg g^{-1}, locally higher) can be found in soils containing waste materials from the mining of Zn ores, but may also occur in soils treated with industrial wastes or Cd-rich phosphate fertilizers. Plant Cd is generally <3 μg g^{-1}, but may reach 20 μg g^{-1} or more in the flora of Cd-rich soils. A plant concentration of >100 μg g^{-1} has been proposed as the threshold for hyperaccumulation of this element (van der Ent et al. 2013); such a level is exceptional, even on a Cd-contaminated site. However, on some Zn-Pb mine waste sites in the south of France and in Slovenia, *Noccaea* species such as *N. caerulescens* and *N. praecox* have been found to typically contain >100 μg g^{-1} Cd, and >1000 μg g^{-1} locally, with very large variations existing among sites and populations, and considerable intra-site variability (Robinson et al. 1998; Escarré et al. 2000; Lombi et al. 2000; Reeves et al. 2001; Schwartz et al. 2006). Similar observations have been made for *Arabidopsis halleri* in Europe (Bert et al. 2002) and for *Sedum alfredii* (Crassulaceae) and *Viola baoshanensis* (Violaceae) in PR China (Liu et al. 2004; Deng et al. 2008). As stressed by van der Ent et al. (2013), further claims of hyperaccumulation of Cd (and other elements) should be restricted to the behaviour of self-sustaining natural populations. Extensive investigations of the behaviour of selected *N. caerulescens* populations have generally been carried out with a focus on phytoremediation rather than agromining (e.g. Chaney et al. 2005).

4.3 Cobalt and Copper

An earlier threshold of 1000 μg g^{-1} for plants to be considered as hyperaccumulators of Cu and Co (Baker and Brooks 1989) has been modified to 300 μg g^{-1} (Krämer 2010; van der Ent et al. 2013) in the light of the apparent rarity of genuine accumulations of these elements in plants. Most reports of Co and Cu exceeding 1000 μg g^{-1} are derived from studies of the metalliferous soils of the Democratic Republic of the Congo, where the two metals occur together at elevated levels in the soils, although in widely varying proportions. Elsewhere, there are local early records of plants having >1000 μg g^{-1} Cu from Cu-mineralized areas (Blissett 1966; Dykeman and De Sousa 1966; Ernst 1966). These reports, and the plant species involved, need more detailed investigation, particularly in view of the potential for soil and dust contamination and the difficulty of its removal from many plant surfaces. The problem is exacerbated in the case of Cu mineral exposures by the common occurrence of more or less pure Cu compounds as secondary mineralization products: a very small amount of such contamination remaining on the plant material can elevate the analytical result considerably. A similar problem arises in the case of plants sampled from the vicinity of smelters.

Normal concentrations of Co and Cu in plants are in the ranges of 0.03–2 μg $g^{-1}$and 5–25 μg g^{-1}, respectively. Plant Cu concentrations are controlled within a remarkably narrow range, even in the presence of high soil Cu; plant Cu concentrations above 100 μg g^{-1} are rare. Even on Co-rich soils, such as those derived from ultramafic rocks, Co in plants rarely exceeds 20 μg g^{-1}. However, the black gum of the southeastern United States (*Nyssa sylvatica* var. *biflora* and var. *sylvatica*) (Nyssaceae) shows exceptional Co accumulation (as much as 845 μg g^{-1}) from normal soils (Beeson et al. 1955; Kubota et al. 1960; Brooks et al. 1977c). Brooks (1977) reported as much as 10,220 μg g^{-1} foliar Co in *Haumaniastrum robertii* (Lamiaceae) from The Democratic Republic of the Congo.

Extensive studies of the vegetation of many sites of mining and smelting activity throughout the Democratic Republic of Congo by F. Malaisse, R. R. Brooks, A.J.M. Baker, and co-workers identified 30 hyperaccumulator plants of Co and 32 of Cu, with 12 species being common to the two lists. The species involved have been summarized and updated in several papers and chapters (Brooks 1977; Malaisse et al. 1979; Brooks et al. 1978, 1980, 1987, 1995; Brooks and Malaisse 1985; Reeves and Baker 2000; Lange et al. 2017). Assessment of these data is difficult for several reasons: (1) numerous changes have been made to the classification and nomenclature of the species involved; (2) uncertainties exist surrounding the pre-treatment of the samples prior to analysis, and in particular the efficacy of the washing regimes; (3) few of the Co- and Cu-accumulating species appear to be absolutely restricted to metalliferous soils, although some have had local or regional uses as indicator plants; (4) there are wide variations in the apparent metal concentrations occurring within many species, even from the same area; (5) there has been a lack of reproducibility in cases where the plants from a given location have been re-examined later; and (6) difficulties have been reported in attempting to reproduce the metal accumulating behaviour in plants in cultivation. A detailed re-assessment of several putative hyperaccumulators was presented by Faucon et al. (2007), who concluded that at least part of the previously reported elevated metal levels could be ascribed to inefficient washing of sample materials prior to analysis. However, in spite of the suspicion that the last of these possibilities is sometimes relevant, many records of Cu and Co hyperaccumulation represent some degree of abnormal uptake by the plant from the soil: Malaisse et al. (1994), for example, have presented iron data that indicate little likelihood of soil contamination (e.g. *Anisopappus davyi* (Asteraceae) with 3504 μg g^{-1} Cu, 3 μg g^{-1} Co, and 67 μg g^{-1} iron). A re-examination of putative Cu hyperaccumulation by *Millotia myosotidifolia* (Asteraceae) from a Cu mine site in South Australia (R.D. Reeves, unpublished data), has not supported the earlier finding of 4% Cu in the plant ash or 2400 μg g^{-1} in the leaves (Blissett 1966), but instead showed Cu levels averaging 516 μg g^{-1}. This concentration is still abnormally high, and much higher than found in other species from the same site, apart from *Arctotheca calendula* (Asteraceae) that averaged 779 μg g^{-1} Cu. Extensive analyses of plants from some unusually Cu-rich ultramafic soils in Malaysia and Brazil have not shown any instance of Cu concentrations reaching 300 μg g^{-1} (van der Ent and Reeves 2015).

Even with the adoption of a 300 μg g^{-1} threshold in defining hyperaccumulation of Cu and Co, and with the addition of reports of Cu accumulation from Sri Lanka, China and Indonesia, we conclude that Cu and Co hyperaccumulation is very rare. From the point of view of agromining applications, it is scarcely relevant whether the threshold is set at 300 or 1000 μg g^{-1}, because the levels of 5000–10,000 μg g^{-1} of interest for agromining of these elements have rarely, if ever, been observed. The high specificity of Ni hyperaccumulation, relative to uptake of Co by Ni accumulator plants on ultramafic soils, also implies that extracting Co as a by-product of Ni agromining will rarely be economically feasible.

4.4 Manganese

Jaffré (1977, 1979, 1980) found that 98 out of 445 species (22%) growing on ultramafic soils of New Caledonia had mean Mn concentrations above 1000 μg g^{-1}; six species had means exceeding 10,000 μg g^{-1}, and nine had at least one specimen above this level. The Mn concentrations within these soils ranged from about 1000–5000 μg g^{-1}, only a little above the range determined for many types of soils worldwide. Recognizing that normal levels of Mn in plant dry matter fall within the rather wide range of 20–500 μg g^{-1}, Baker and Brooks (1989) chose a level of 10,000 μg g^{-1} to define Mn hyperaccumulation. This criterion has been maintained in the review by van der Ent et al. (2013). After accounting for synonymies and changes of nomenclature for several species, data are now available for 24 species that have been found to meet this threshold in at least one specimen. These include a single species of *Alyxia* (Apocynaceae), *Beaupreopsis*, and *Grevillea* (Proteaceae) (Jaffré 1977, 1979; Losfeld et al. 2015), all from New Caledonia; *Chengiopanax* and *Tieghemopanax* (Araliaceae) from Japan and New Caledonia, respectively (Mizuno et al. 2008; Losfeld et al. 2015); *Garcinia* (Clusiaceae) from New Caledonia (Jaffré 1980); two species each of *Phytolacca* (Phytolaccaceae) (Xue et al. 2004); and *Polygonum* (Polygonaceae) from China (Deng et al. 2010; Liu et al. 2016), three species of *Denhamia* (formerly in *Maytenus*—Celastraceae), from New Caledonia and Australia, (Jaffré 1977;

Fernando 2008), two of *Virotia* (formerly in *Macadamia*—Proteaceae) from New Caledonia (Jaffré 1979), and nine of *Gossia* (formerly in *Austromyrtus* and *Eugenia*—Myrtaceae) from eastern Australia (Bidwell et al. 2002; Fernando et al. 2008, 2009; Jaffré 1980; Losfeld et al. 2015). Because of the extreme levels of Mn, locally reaching 2–5% in dry matter in some of these species, the plant ash may contain 10–25% Mn, which should make agromining for Mn worthy of further study and field trials.

4.5 Chromium

Even on ultramafic soils having high chromium (Cr) concentrations (500–5000 μg g^{-1}) it is normal to find Cr concentrations in plant material in the range of 1–30 μg g^{-1}. Occasional reports of much higher concentrations are believed to reflect contamination by wind-blown dusts or smelter fallout, or analytical problems. In fact, high Cr concentrations in plants from ultramafic soils have been used as an indicator of soil contamination (see, e.g. Jaffré et al. 1979b; Brooks and Yang 1984). In the absence of evidence for consistently high Cr concentrations existing in any species, there seems to be little hope of finding a future for agromining of this element.

4.6 Selenium

Selenium is essential for animal and human health, and exhibits a narrow range between the levels required to prevent deficiency diseases and those that produce symptoms of toxicity. The Se content of soils is typically below 2 μg g^{-1}, but can reach several hundred μg g^{-1} in soils derived from certain Cretaceous shales. In plant dry matter, Se concentrations are generally below 1 μg g^{-1}, and may even be <0.01 μg g^{-1} in areas of Se-poor soils. However, the accumulation of Se to high levels (locally >1000 μg g^{-1}) by legumes in the genus *Astragalus* (Fabaceae) from seleniferous soils in the western United States was found to be responsible for poisoning of livestock (Byers et al. 1938).

A detailed account of the discovery of Se-accumulating plants in the western United States can be found elsewhere (Rosenfeld and Beath 1964). Reeves and Baker (2000) tabulated values and references for 20 species that have shown maximum Se concentrations above 1000 μg g^{-1}. Because of the very low levels of Se that normally occur in plants, a case can be made (Reeves 2005; van der Ent et al. 2013) for taking 100 μg g^{-1} as the threshold for Se hyperaccumulators. The use of plants showing some degree of Se accumulation for economic extraction of elemental Se has not yet been proposed. However, there are potential applications in: (1) phytoremediation of soils that have become Se-contaminated through extensive use of Se-rich irrigation waters (Parker et al. 2003), (2) harvesting crop plants suitable for stock feed from high-Se areas and transport of this material to areas of Se deficiency (Bañuelos and Mayland 2000), and (3) Se biofortification for improving human health (Bañuelos et al. 2014).

4.7 Arsenic

Normal As concentrations in igneous rocks and soils are in the range of 1–10 μg g^{-1}. Higher soil As concentrations can be found in areas of polymetallic sulphide mineralization and of some pyritic black shales, in places contaminated through the smelting of chalcophile element ores, in areas of geothermal activity, and where As compounds have been used as horticultural sprays or timber preservation agents. Plant As concentrations are normally on the order of 1 μg g^{-1}, but higher values can be found in contaminated areas. As hyperaccumulation (based on a 1000 μg g^{-1} dry matter criterion) has been known for more than 50 years. Warren et al. (1964) found As in the ash of growing tips of Douglas fir (*Pseudotsuga menziesii*) to be 2500–10,000 μg g^{-1} over soils containing 1000–5000 μg g^{-1} As. The highest of these values almost certainly corresponds to >1000 μg g^{-1} on a dry weight basis.

Studies by several groups on the behaviour of aquatic plants in the Waikato River in the North Island of New Zealand showed that three aquatic plants act as As hyperaccumulators. Natural geothermal activity, together with borefield drainage and waste water from the Wairakei geothermal power plant that opened in 1953, combined to raise the As concentration in the river from ca. 0.01 mg L^{-1} to as much as 0.08–0.09 mg L^{-1} before dilution and sedimentation processes lower the concentrations downstream. The adventive aquatic weeds *Ceratophyllum demersum* (Ceratophyllaceae), *Egeria densa,* and *Lagarosiphon major* (Hydrocharitaceae) act as As hyperaccumulators (Lancaster et al. 1971; Aggett and Aspell 1980; Liddle 1982; Reeves and Liddle 1986), yielding As concentrations in the plant dry matter from ca. 100 μg g^{-1} to 1000–1500 μg g^{-1}. The bioaccumulation factor, taken as the plant/substrate concentration quotient, can be as high as 30,000, e.g. where the plants contain 1500 μg g^{-1} in water with 0.05 mg L^{-1} As.

More recent attention has been paid to As accumulation by fern species, particularly those growing in areas of As contamination from waste disposal related to timber preservation processes or mining. Ma et al. (2001) reported As at 3280–4980 μg g^{-1} in *Pteris vittata* (Pteridaceae) plants from soils containing 19–1603 μg g^{-1} As. As hyperaccumulation was also found by Vittoottiviseth et al. (2002) in the fern *Pityrogramma calomelanos* (Pteridaceae). A number of fern species may possess this capability of As accumulation as a constitutive property (Meharg 2002). However, applications of As hyperaccumulators seem likely to lie more in the area of remediation of As-contaminated waters and land, rather than in economic extraction of the As itself.

4.8 Thallium

Currently only a small number of thallium (Tl) hyperaccumulator plants have been reported, mainly from France: *Biscutella laevigata* (Brassicaceae) with up to 15,200 μg g^{-1} Tl (Anderson et al. 1999), and *Iberis intermedia* (Brassicaceae) (now regarded as a synonym of *I. linifolia*) with up to 2810 μg g^{-1} Tl (LaCoste et al. 1999; Leblanc et al. 1999). Van der Ent et al. (2013) proposed a threshold value of 100 μg g^{-1} to define Tl hyperaccumulation. The substantial value of Tl metal might justify Tl agromining, but the locations at which this could take place appear to be rather limited.

5 Hyperaccumulators, Phytoremediation, and Agromining

Major potential uses of hyperaccumulator plants focus on the possibility of removal of large amounts of a particular element from the soil without significant chemical intervention, other than the application of conventional fertilizers. Such uses include phytoremediation (removal of an undesirable metal to restore contaminated soil for any of a variety of uses), and agromining (plant extraction of elements to provide a feedstock from which a valuable metal, or one of its compounds, can be extracted economically). For these purposes, important factors are the rate of biomass production and the concentration of the desired element that can be achieved in harvestable plant matter.

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