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Current status and challenges in developing nickel phytomining: an agronomic perspective

Philip Nti Nkrumah · Alan J. M. Baker · Rufus L. Chaney · Peter D. Erskine · Guillaume Echevarria · Jean Louis Morel · Antony van der Ent

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Abstract

Background Nickel (Ni) phytomining operations cultivate hyperaccumulator plants ('metal crops') on Ni-rich (ultramafic) soils, followed by harvesting and incineration of the biomass to produce a high-grade 'bio-ore' from which Ni metal or pure Ni salts are recovered.

Scope This review examines the current status, progress and challenges in the development of Ni phytomining agronomy since the first field trial over two decades ago. To date, the agronomy

of less than 10 species has been tested, while most research focussed on *Alyssum murale* and *A. corsicum*. Nickel phytomining trials have so far been undertaken in Albania, Canada, France, Italy, New Zealand, Spain and USA using ultramafic or Ni-contaminated soils with 0.05–1 % total Ni.

Conclusions N, P and K fertilisation significantly increases the biomass of Ni hyperaccumulator plants, and causes negligible dilution in shoot Ni concentration. Organic matter additions have pronounced positive effects on the biomass of Ni hyperaccumulator plants, but may reduce shoot Ni concentration. Soil pH adjustments, S additions, N fertilisation, and bacterial inoculation generally increase Ni phytoavailability, and consequently, Ni yield in 'metal crops'. Calcium soil amendments are necessary because substantial amounts of Ca are removed through the harvesting of 'bio-ore'. Organic amendments generally improve the physical properties of ultramafic soil, and soil moisture has a pronounced positive effect on Ni yield. Repeated 'metal crop' harvesting depletes soil phytoavailable Ni, but also promotes transfer of non-labile soil Ni to phytoavailable forms. Traditional chemical soil extractants used to estimate phytoavailability of trace elements are of limited use to predict Ni phytoavailability to 'metal crop' species and hence Ni uptake.

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Keywords Agronomy · Annual Ni yield · Biomass production · Economic Ni phytomining · Ni hyperaccumulator plants · Ultramafic soils

Introduction

Phytomining operations cultivate hyperaccumulator plants on low-grade ore bodies or superficially mineralised (ultramafic) soils, followed by harvesting and a series of post-harvest processing operations to recover target elements such as nickel (Ni) for profit (Anderson et al. 1999; Chaney et al. 1998; Hunt 2014; Robinson et al. 1999a; van der Ent et al. 2015). Appropriate agronomic practises are a critical pre-requisite in the development of commercially viable phytomining technology (Li et al. 2003a; Rascio and Navari-Izzo 2011). Numerous agronomic experiments have been undertaken since the first phytomining field trial in 1995 and these studies have substantially advanced our understanding on phytomining agronomy (Bani et al. 2015a; Chaney et al. 2007b; Li et al. 2003a; Nicks and Chambers 1995; Robinson et al. 1997a). This review examines the current status of knowledge on Ni phytomining agronomy since the first field trial, and identifies future challenges and research priorities.

Nickel phytomining operations

Nickel phytomining operations consist of growing selected hyperaccumulator plant species ('metal crops') on Ni-rich (ultramafic) soils, followed by harvesting and incineration of the biomass to produce a 'bio-ore' from which Ni salts or Ni metal may be recovered (Anderson et al. 1999; Chaney et al. 1998; Hunt 2014; Robinson et al. 1999b). These operations may be undertaken on: (i) large ultramafic areas with suitable topography, where soils are unsuitable for food production; or (ii) degraded Ni-rich land which includes Ni laterite mine sites, smelter contaminated areas and ore beneficiation tailings (van der Ent et al. 2015a). The criteria for selection of 'metal crops' include high biomass yield combined with high Ni concentrations (>1 %) in the above-ground biomass (Chaney et al. 2007a). Local plant species are recommended because of their adaptation to local climatic and edaphic conditions (Baker 1999). Suitable species must be relatively easy to collect as bulk seed accessions and have high success rates of germination, establishment and growth (O'Dell and Claassen 2009). The selected species may be propagated via direct seeding, transplantation, or by using cuttings (Brooks et al. 1998; Li et al. 2003a). Appropriate soil

and plant management practices, based on insights from laboratory and field tests, are required to maximise the yields of the selected 'metal crop'. Annual Ni yields ranging from 67.5 to 168 kg ha⁻¹ have been demonstrated in phytomining field trials (Bani et al. 2015a; Bani et al. 2015b; Robinson et al. 1997a; Robinson et al. 1997b). In principle, Ni phytomining has similar costs of production as food crops such as corn (Chaney et al. 2007a); and this potentially makes Ni phytomining a viable business opportunity for 'metal farmers' especially in developing countries such as Indonesia (van der Ent et al. 2013b).

Economics of Ni phytomining

Here we present the economic potential of Ni phytomining under two generalised production systems: an intensive system such as demonstrated in the USA (e.g. Li et al. 2003a) and an extensive system as demonstrated in Albania (e.g. Bani et al. 2015a). In the intensive system, the cost of production is high, including costs for seed stock, fertilisers, labor and equipment, whereas the production costs in the extensive system are relatively low because it mainly involves the use of fertilisers, herbicides and complementary agricultural management practices. On the basis of: (i) an average commercial value of Ni over a period of 5 years (2010–2015) at the London Metal Exchange of \$18 per kg, (ii) an annual crop Ni yield of 200 kg ha⁻¹ for an intensive system and 110 kg ha⁻¹ for an extensive system, (iii) a cost of production in 2016 of \$1074 ha⁻¹ yr⁻¹ and \$600 ha⁻¹ yr⁻¹ for the intensive and extensive systems, respectively, (iv) an estimated 20 % of Ni value for the cost of metal recovery, then the gross values of an annual phytomining crop per ha for intensive and an extensive system are \$3600 and \$1980, respectively, with corresponding net values of \$1806 and \$984. It is hence clear that Ni phytomining is a highly profitable agricultural technology for the respective systems. Other potential sources that may further increase the profitability of Ni phytomining include: i) recovery of energy of combustion and ii) sale of carbon credits. Although a Ni metal product is in itself profitable, other higher value Ni products, including pure Ni salts, may further increase the profitability of Ni phytomining, but the current market for pure Ni salts is limited.

Soil Ni availability for ‘metal crops’

Ultramafic soils develop from the weathering of ultramafic bedrock (Baillie et al. 2000; Brooks 1987; Li et al. 2003a; Tappero et al. 2007) and are characterised by relatively high concentrations of Mg, Fe, Cr, Co, Mn and Ni, usually low concentrations of Ca, low to deficient levels of macronutrients (N, P and K), and deficient levels of Mo and B (Baker and Brooks 1989; Brooks 1987; Jenny 1980; Kruckeberg 1985; Proctor and Woodell 1975). The soil pH of many ultramafic soils, especially those derived from strongly serpentinised bedrock, is often relatively high due to the buffering of Mg-silicates (Alexander 2004; Chardot et al. 2007). The soil pH can range from neutral to alkaline with a pH ranging from 6–8 in Mediterranean climates and in young soils (Cambisols) (Massoura et al. 2006), whereas in tropical regions with intensive leaching, the soil pH may be acidic (pH 5.5) on Ferralsols (‘laterites’) (van der Ent et al. 2013b). Total Ni concentrations in ultramafic surface soils typically range from 0.1 to 0.3 % but is often strongly enriched in the underlying saprolite (0.8–1.5 %), especially under intense leaching under tropical conditions (Estrade et al. 2015; Golightly 1979; Proctor and Nagy 1992; Quantin et al. 2002). Ultramafic soils that have total Ni concentrations greater than 0.1 % with high phytoavailable Ni pools are potentially suitable for Ni phytomining (van der Ent et al. 2015b).

Nickel in ultramafic soils is associated with three main fractions: (i) short-term labile fraction (water-soluble fraction, NH_4 -acetate-exchangeable fraction, exchangeable from Mn-oxides and amorphous Fe-oxides); (ii) long-term labile fraction (bound to crystalline Fe-oxides and adsorbed to organic matter); and (iii) non-labile fraction (solid phase residual fraction including Ni-Al layered double hydroxides, Ni-silicates and Ni occluded in Fe and Mn oxides), the latter generally constitutes >50 % of the soil total Ni content (Cheng et al. 2011; Hseu 2006; Quantin et al. 2002; Tessier et al. 1979; Viets 1962; Vithanage et al. 2014). Soil Ni availability is mainly controlled by the mineralogy and Ni-bearing mineral phases (Becquer et al. 2001; Chardot et al. 2007; Quantin et al. 2001). In strongly leached ultramafic soils, such as in Ferralsols, generally the Ni phytoavailability is low (Bani et al. 2014; Cheng et al. 2011; Das et al. 1999; Echevarria et al. 2006; Massoura et al. 2006; Raous et al. 2010; Raous et al. 2013). However, in clay-mineral rich young soils (Cambisols)

and saprolite materials, the Ni phytoavailable fraction is generally high (Raous et al. 2010). The main factors that influence Ni phytoavailability include: (i) the original parent material characteristics and its weathering history; (ii) soil composition, such as organic matter and clay content, thermodynamic conditions including pH and redox potential, and (iii) rhizosphere effects including root exudates (Antić-Mladenović et al. 2011; Baker and Walker 1989; Chardot et al. 2007; Echevarria et al. 1998; Echevarria et al. 2006; Ernst 1996; Massoura et al. 2006; Massoura et al. 2004). High nickel phytoavailability is essential for successful Ni phytomining (Massoura et al. 2004), as Ni hyperaccumulator plants take up Ni from the same soil labile Ni pools as ‘normal’ plants (Echevarria et al. 2006; Shallari et al. 2001). Nickel hyperaccumulator plants have efficient root absorption mechanisms that deplete the phytoavailable Ni pools to the extent that the soil Ni chemical equilibrium is changed (Centofanti et al. 2012; Deng et al. 2014). As a result, Ni from non-labile pools replenishes the labile pool over time to maintain equilibration (Centofanti et al. 2012), but this is a slow process and depends on the local buffering system (Massoura et al. 2004).

Several different chemical extraction methods permit measuring soil Ni labile pools. These are illustrated in Fig. 1a, b providing data for the DTPA- and NH_4 -acetate-extractable Ni of 17 ultramafic soils from Oregon and Maryland, USA, which have been acidified by addition of HNO_3 and leaching of dissolved cations before fertilisation with N, P, K, CaSO_4 , B and Mo and cropped with *Alyssum* species (Chaney et al. unpublished). Figure 1c shows the accumulation of Ni in shoots of *A. murale* and *A. corsicum* on 17 of the same topsoils after growing *Alyssum* for 120 days from transplanting. It is clear that the effect of pH on extractability is not closely related to the effect of pH on accumulation of Ni in shoots of *Alyssum* species and these usual soil extraction methods are not predictive of Ni accumulation by *Alyssum* species. Traditional soil extraction methods cannot be used for prediction of Ni accumulation by hyperaccumulator plants, even though several authors have previously used NH_4 -acetate extraction to predict the depletion of Ni by phytoextraction, or to compare varied soils as a phytomining resource (e.g. Robinson et al. 2003; Robinson et al. 1999b). The Isotopic Exchange Kinetics (IEK) method allows for the description of the magnitude of the Ni labile pool (Echevarria et al. 1998) but

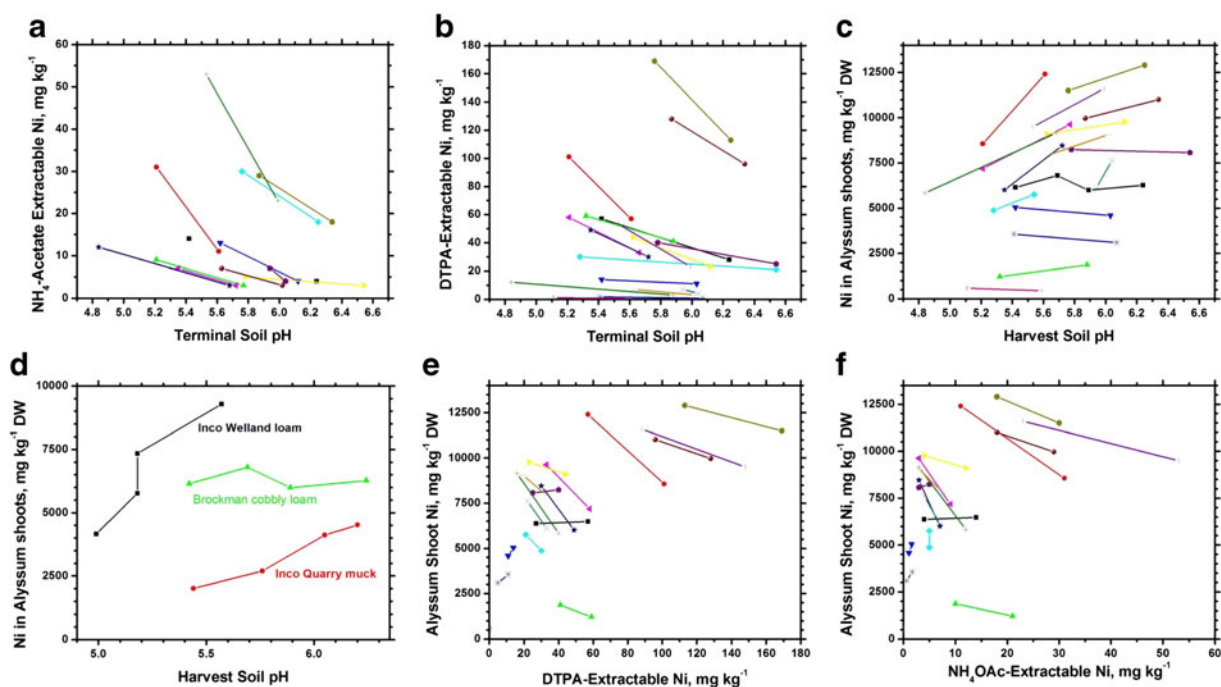


Fig. 1 The effect of adjusted pH on (a) 1.0 M NH_4 -acetate-extractable; (b) DTPA-extractable Ni; and (c) Ni accumulation in shoots of *Alyssum* species grown for 120 days in 17 ultramafic soils from Oregon and Maryland, USA. (d) Effect of pH on Ni accumulation in shoots of *Alyssum* species grown for 120 days on 2 soils collected near a Ni refinery at Port Colborne, Ontario (Quarry muck; Welland loam; organic and mineral soils respectively), and the Brockman cobbly loam. (e) The effect of adjusted

pH (control treatment 2, and acidified treatment 6, which have been described in Table 3) on 1.0 M NH_4 -acetate-extractable and, (f) DTPA-extractable Ni in relation to Ni phytoextraction from 17 ultramafic soils from Oregon and Maryland, USA. Soil pH was adjusted by addition of HNO_3 , followed by leaching of soluble ions, and fertilization for the growth of *Alyssum* species to test the effect of soil pH on Ni accumulation

may not describe the supply of Ni from the soil for uptake in hyperaccumulator plants. Currently no chemical extraction method can accurately predict Ni availability, and hence uptake to hyperaccumulator plants.

Nickel hyperaccumulator plants as ‘metal crops’

More than 400 Ni hyperaccumulator plants across over 40 families have been recorded worldwide (Krämer 2010; Pollard 2002; van der Ent et al. 2013a; Verbruggen et al. 2009). The greatest numbers of hyperaccumulator plant species are known from Cuba, New Caledonia and Southeast Asia (Reeves et al. 1999). However, species of Brassicaceae from the Mediterranean Region are the most widely studied for their Ni phytomining potential (Bani et al. 2015a; Chaney et al. 2007a). Most Ni hyperaccumulator plants accumulate 0.1–0.5 % Ni in their biomass, but for phytomining only so-called ‘hypernickelophores’ (>1 % Ni) are

potentially suitable (Chaney et al. 2007a; b; van der Ent et al. 2013a). Table 1 lists the Ni ‘hypernickelophore’ species that have been identified as having especially high Ni phytomining potential for use as ‘metal crops’.

Field and laboratory agronomic trials to optimise Ni phytomining

Nutrient management to increase biomass production

Since the first field trial on a farmed ultramafic soil in California (USA), using *Streptanthus polygaloides* without any fertiliser application (Nicks and Chambers 1995), all other reported trials have incorporated nutrient management. Due to the deficiency of macronutrients in ultramafic soils, there is a strong positive response of biomass production to fertilisation in *Alyssum* spp. (Bani et al. 2015a). The hyperaccumulator species

tested on ultramafic soils have proven to react strongly to increasing levels of soil N, P and K, due to the very low fertility of their native habitats. Trials using ultramafic soils have shown that fertiliser application enhances shoot biomass production of Ni hyperaccumulator plants and also increases their overall Ni yield (Table 2). As such, N+P+K fertilisation tripled the biomass of *Berkheya coddii* dry matter to 9 t ha⁻¹ (Robinson et al. 1999a). There was also a significant increase in the biomass of *Alyssum murale* from 3.2 t ha⁻¹ in unfertilised plots to 6.3 t ha⁻¹ in the fertilised treatment (Bani et al. 2013). Table 3 shows the effect of P and Ca fertilisers and pH adjustment on Ni and other element accumulation by *A. murale* from an Oregon ultramafic soil that had received little fertiliser from previous land use. Trials on the independent effect of N application indicate significant increases in *Alyssum* biomass with negligible effect on the shoot Ni concentration, subsequently increasing Ni yield (Bennett et al. 1998; Li et al. 2003a). A significant effect on biomass production has been observed for N application (Bennett et al. 1998; Li et al. 2003a), whereas that for P has been negligible if soils had been fertilized for crop production previously (Bani 2007; Bani et al. 2015a). However, split N application could be employed to minimise excessive N leaching (Li et al. 2003a). The Ni content of *B. coddii* increased two-fold with N addition (Robinson et al. 1997a), whilst split N application also increased annual biomass Ni yields (Bani et al. 2015a; Chaney et al. 2007a). Phosphorus has a particularly strong effect on the biomass yield and Ni uptake by hyperaccumulator species growing on soil not previously fertilized (Table 3) while previously fertilized soils show a lesser response to P fertilizer (Bennett et al. 1998; Chaney et al. 2008; Robinson et al. 1997a; Shallari et al. 2001). Additions of micronutrients have also been considered during fertilisation trials because ultramafic soils are usually deficient in B and Mo (Li et al. 2003b). Some ultramafic soils rich in Fe have proven deficient in Mo even for native ultramafic vegetation (Walker 1948; Walker 2001), while low levels of B fertilisers may be beneficial in many previously unfertilized soils.

The effects of soil pH adjustments on Ni accumulation

Studies indicate that the uptake of Ni from ultramafic soils by Ni hyperaccumulator plants is strongly influenced by soil pH (Chaney et al. 1998; Chaney et al.

Table 1 Nickel hyperaccumulator species with over 1 % Ni ('hypernickelophores') which have high potential for application as 'metal crops' in Ni phytomining operations

Species	Potential application area	Native distribution	Height (m)	Cropping system	Shoot Ni (%)	References
<i>Alyssum</i> spp.	Mediterranean and Eurasian Region	S & SE Europe, Turkey, Armenia, Iraq, Syria	0.5–1	Perennial herb	1–2.5	(Brooks 1998)
<i>Leptoplax</i> spp.	Mediterranean and Eurasian Region	Greece	1–1.5	Perennial herb	1–3.5	(Reeves et al. 1980)
<i>Bornmuellera</i> spp.	Mediterranean and Eurasian Region	Greece, Albania, Turkey	0.3–0.5	Perennial herb	1–3	(Reeves et al. 1983)
<i>Buxus</i> spp.	Tropical Central America	Cuba	0.3–12	Ligneous shrub	1–2.5	(Reeves et al. 1996)
<i>Leucocroton</i> spp.	Tropical Central America	Cuba	1–3.3	Ligneous shrub	1–2.7	(Reeves et al. 1996)
<i>Phyllanthus</i> spp.	Tropical Asia-Pacific Region	Southeast Asia and Central America	1–6	Ligneous shrub	2–6	(Baker et al. 1992; van der Ent et al. 2015b)
<i>Rimorea bengalensis</i>	Tropical Asia-Pacific Region	Southeast Asia	5–20	Ligneous shrub	1–2.7	(Brooks and Withier 1977; Jopony and Tongkul 2011)
<i>Berkheya coddii</i>	Southern Africa	South Africa, Zimbabwe	1–2	Perennial herb	1.1	(Morrey et al. 1989)
<i>Pearsonia metallifera</i>	Southern Africa	Zimbabwe	0.35–1.5	Perennial herb	1.4	(Wild 1974)

Table 2 Outcomes of Ni phytomining agronomic trials showing that N + P + K fertilisation and organic matter additions significantly increase the biomass of Ni hyperaccumulator plants, with the former causing negligible dilution in shoot Ni concentrations whereas the latter may reduce it. Plant growth regulators increase the biomass of Ni hyperaccumulator plants, but the effect on Ni yield is not clear. In addition, soil pH adjustment, S addition, N fertilisation, and bacterial inoculation increase uptake and accumulation of Ni shoots in Ni hyperaccumulator species

Agronomic practices	Species	Field and/or pot trials	Locations	Substrates	Effects on Ni yield	References
N + P + K fertilisation	<i>Alyssum bertolonii</i> , <i>Berkheya coddii</i> , <i>Sreptanthus polygaloides</i> <i>Alyssum murale</i> <i>Alyssum serpyllifolium</i> ssp. <i>Lusitanicum</i> , <i>A. serpyllifolium</i> ssp. <i>malactitanum</i> , <i>Noccaea goosingense</i> <i>Berkheya coddii</i>	Field trial Pot trials	Tuscany (Italy) New Zealand Pogradec (East of Albania) Spain	Ultramafic soil 3 : 1 mixture of bark: crushed serpentine rock	Increases Ni yield by increasing biomass production while causing negligible dilution in shoot Ni	(Álvarez-López et al. 2016; Bani et al. 2015a; Bennett et al. 1998; Robinson et al. 1997a; Robinson et al. 1997b)
Sulphur addition	<i>Alyssum murale</i> <i>Alyssum corsicum</i>	Pot trials	Palmerston North, New Zealand	1:1 ultramafic soil : pumice soil mixture	Increases Ni yield by increasing Ni phytoavailability	(Robinson et al. 1999b)
Soil pH adjustment	<i>Alyssum murale</i> <i>Alyssum corsicum</i>	Pot trials	Ontario, Canada	Ni refinery contaminated soil (Welland loam and Quarry muck)	Increases Ni yield while decreasing Ni extractability	(Kukier et al. 2004; Li et al. 2003b)
Different substrates on the basis of soil Ni phytoavailability	<i>Leptoplax emarginata</i> <i>Bornmuellera tymphaea</i> <i>Thlaspi caerulescens</i>	Pot trials	France	Ultramafic soil Ultramafic soil agricultural Calcaric Cambisol acid agricultural soil (Haplic Luvisol)	High Ni phytoavailability increases Ni yield	(Chardot et al. 2005)
Bacterial inoculation	<i>Alyssum murale</i> <i>Alyssum murale</i> + <i>Noccaea tymphaea</i> <i>Bornmuellera tymphaea</i> + <i>N. tymphaea</i>	Pot trials	Oregon, USA France	Ultramafic soil	Increases Ni yield by increasing Ni uptake and biomass production	(Abou-Shanab et al. 2006; Durand et al. 2015)
Plant growth regulators	<i>Alyssum corsicum</i> <i>Alyssum malactitanum</i> <i>Alyssum murale</i> <i>Noccaea goosingense</i> <i>Alyssum murale</i>	Pot trials	Spain	Ultramafic soil	Positive effects on biomass, but the effects on Ni yield is not clear	(Cabello-Conejo et al. 2014)
Weed control	<i>Alyssum murale</i>	Field trial	Pogradec, East of Albania	Ultramafic soil	Enhances Ni yield by reducing competition for essential nutrients and water between the 'metal crop' and weeds	(Bani et al. 2015a)
Plant density	<i>Alyssum murale</i>	Field trial	Pojakë and Dornosdovë, Albania	Ultramafic soil	Optimum plant density increases Ni yield	(Bani et al. 2015b)
Organic matter additions	<i>Alyssum serpyllifolium</i> ssp. <i>lusitanicum</i> <i>A. serpyllifolium</i> ssp. <i>malactitanum</i> , <i>Alyssum bertolonii</i> <i>Noccaea goosingense</i>	Pot trial	Spain	Ultramafic soil	Increases Ni yield by significantly increasing shoot biomass although shoot Ni concentration decreases	(Álvarez-López et al. 2016)

Table 3 Effect of amending Brockman cobbly loam ultramafic soil (fine, magnesian, mesic Vertic Haploxerepts) from a unmanaged pasture field in Josephine County, Oregon, USA with phosphate (kg ha^{-1} P), pH adjusting, or Ca fertiliser ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$, t ha^{-1}) treatments on terminal soil pH, mean yield and macronutrient composition of shoots of two *Alyssum* species (*A. murale* and *A. corsicum*) grown for 120 days (GM designates geometric mean). For single variable treatments, all other nutrients were applied as

in treatment 2 (100 kg ha^{-1} P; $1.0 \text{ t CaSO}_4 \cdot 2\text{H}_2\text{O ha}^{-1}$). Bray-1 extractable P was 0.49, 11.1, 49.9 and 100 mg kg^{-1} soil for the 0, 100, 250 and 500 kg ha^{-1} P treatments (applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$); all except treatment 1 received 200 kg ha^{-1} N as NH_4NO_3 . The experimental design, set-up and conditions have been described by Li et al. (2003b) in which the data from the Port Colborne soils were reported similar to the serpentine soil treatments

Treatment		Final pH g pot^{-1}	GM-Yield	GM-P g kg^{-1}	Mg	Ca	K
1	None	6.56 a ‡	4.1 c	1.04 e	4.06 d	17.5 ab	9.1 d
Phosphate treatments:							
3	0 P	5.82 e	1.6 d	0.61 f	6.47 a	17.5 ab	10.0 cd
2	100 P	6.24 b	24.5 a	2.16 cd	6.20 bc	17.1 ab	16.5 b
4	250 P	6.14 bcd	23.2 ab	3.00 b	6.46 bc	19.8 a	19.9 a
5	500 P	6.16 bc	26.5 a	3.59 a	6.40 bc	18.2 ab	19.8 a
pH treatments:							
6	Lo pH	5.42 g	27.4 a	2.03 d	4.92 cd	16.7 ab	18.4 ab
7	MLo pH	5.69 f	26.2 a	2.12 d	6.42 bc	18.5 ab	17.0 b
8	MHi pH	5.89 e	27.0 a	2.07 d	5.31 bcd	16.2 ab	18.4 ab
2	As is pH	6.24 b	24.5 a	2.16 cd	6.20 bc	17.1 ab	16.5 b
Ca:Mg treatments:							
9	0.0 Ca	6.10 cd	19.3 b	2.43 c	5.66 bc	14.8 b	12.4 c
2	1.0 Ca	6.24 b	24.5 a	2.16 cd	6.20 bc	17.1 ab	16.5 b
10	2.5 Ca	6.04 cd	25.2 a	2.10 d	6.74 b	18.4 ab	17.7 ab
11	5.0 Ca	6.03 d	24.2 a	1.94 d	6.26 bc	16.2 ab	17.2 ab

‡ Means followed by the same letter are not significantly different ($P < 0.05$ level) according to the Duncan-Waller K-ratio t-test

2007b; Chaney et al. 2000; Chardot et al. 2005; Echevarria et al. 2006). In both strongly acidic and alkaline soil conditions, Ni uptake is low in ultramafic soils (Table 4; Fig. 1c), but not in smelter contaminated soils (Fig. 1d) (Chaney et al. 2007a; Robinson et al. 1999b; Robinson et al. 1997a). The solubility of Ni, as well as that of other divalent cations including Zn, Cu, Fe, Co and Mn, generally increases in acidic soil conditions (Chaney et al. 2007b; Robinson et al. 1996). On the other hand, at relatively high soil pH, the concentration of Fe-oxides in ultramafic soils increases the sorption of Ni (Chaney et al. 2007a) limiting Ni availability which ultimately leads to a reduced Ni uptake in hyperaccumulator plants. Smelter contaminated soils low in Fe-oxides showed an increase in *Alyssum* species (*A. murale* and *A. corsicum*) shoot Ni concentration across the range from about pH 5 to 7 or higher, while ultramafic soils revealed a maximum shoot Ni near pH 6.5 (Table 4; Fig. 1c). Indeed, Ni

uptake decreased at elevated soil pH when both *B. coddii* and *A. bertolonii* were grown in ultramafic soils (Robinson et al. 1999b; Robinson et al. 1997b). Within a pH range of 5–6.5 in ultramafic soils, Ni accumulation by Ni hyperaccumulator plants increases (Chaney et al. 2007b). Because of the different effects of soil pH on extractability of soil Ni and uptake by *Alyssum* species, it is not possible to accurately predict shoot Ni from extractable Ni data (Fig 1e,f). On the other hand, when Ni accumulation from 17 ultramafic topsoils was regressed (linear or quadratic) on to the total soil Ni or DTPA-extractable Ni, the DTPA-extractable Ni had R^2 0.47 for linear and R^2 0.53 for quadratic regressions, but soil total Ni had R^2 0.65 for linear and R^2 0.72 for quadratic regression of shoot Ni (Fig. 2). Higher soil Ni will always be a desired property of soils intended for commercial phytomining. More research is required for assessing the ways in which hyperaccumulator plants access Ni pools in the soil,

Table 4 Effect on terminal soil pH, mean yield and microelement composition of shoots of *Alyssum* species grown for 120 days (GM designates geometric mean) under conditions noted in Table 3

Treatment		Final pH g pot ⁻¹	GM-Yield	GM-Ni mg kg ⁻¹	GM-Co	GM-Mn	GM-Zn	GM-Fe	Cu
1	None	6.56 a ‡	4.1 c	14,740. a	34.3 c	56.5 e	63.4 bc	154. b	3.0 cd
Phosphate treatments:									
3	0 P	5.82 e	1.6 d	6250. cd	19.4 ef	62.3 cde	118. a	273. a	2.8 d
2	100 P	6.24 b	24.5 a	6270. cd	19.9 ef	60.9 cde	59.9 bc	112. cd	3.6 bc
4	250 P	6.14 bcd	23.2 ab	6810. bc	22.6 def	65.2 cde	60.2 bc	104. d	4.2 ab
5	500 P	6.16 bc	26.5 a	5690. d	18.1 f	67.2 cde	55.1 cd	92. d	4.0 ab
pH treatments:									
6	Lo pH	5.42 g	27.4 a	6150. cd	224. a	462. a	63.1 bc	144. bc	4.4 ab
7	MLo pH	5.69 f	26.2 a	6800. bc	50.4 b	132. b	68.7 b	117. bcd	4.6 a
8	MHi pH	5.89 e	27.0 a	5990. cd	28.8 cd	73.1 cd	58.2 bcd	96. d	3.6 bc
2	As is pH	6.24 b	24.5 a	6270. cd	19.9 ef	60.9 cde	59.9 bc	112. cd	3.6 bc
Ca:Mg treatments:									
9	0.0 Ca	6.10 cd	19.3 b	7860. b	21.1 ef	55.6 e	49.4 d	87. d	3.1 cd
2	1.0 Ca	6.24 b	24.5 a	6270. cd	19.9 ef	60.9 cde	59.9 bc	112. cd	3.6 bc
10	2.5 Ca	6.04 cd	25.2 a	6050. cd	18.4 ef	58.2 de	59.6 bc	87. d	3.8 bc
11	5.0 Ca	6.03 d	24.2 a	5630. d	24.4 de	78.5 c	63.3 bc	93. d	3.6 bc

‡ Means followed by the same letter are not significantly different ($P < 0.05$ level) according to the Duncan-Waller K-ratio t-test.

and to develop predictive tools for Ni uptake in hyperaccumulator plants.

The effects of soil Ca amendments on Ni accumulation

Nickel hyperaccumulator plants accumulate normal foliar levels of Ca from soils with very low concentrations of exchangeable Ca and low Ca:Mg ratios, which is part of the natural adaptation to growing on ultramafic soils (Brooks 1987; Vlamis and Jenny 1948; Walker et al. 1955). Studies show that there is a positive correlation between the exchangeable Ca:Mg ratio and the labile Ni pools in ultramafic soils (Cheng et al. 2011). Calcium supply to high Mg ultramafic soils will be required to maintain the annual Ni uptake in *Alyssum* species because biomass harvest and removal reduces the pool of phytoavailable Ca in these soils, for example, the annual removal of 1 t of biomass removes 20 kg of Ca (Chaney et al. 2007a; Chaney et al. 2008). The sequestration mechanisms for Ni is distinct from Ca handling or storage in Ni hyperaccumulator plants (Broadhurst et al. 2004a); but a positive correlation exists in the foliar concentrations of Ca and Ni in

some ‘metal crop’ species (van der Ent and Mulligan 2015). Nickel hyperaccumulator species absorb more Ca relative to Mg, which leads to high Ca:Mg ratio in the leaf tissues (Bani et al. 2014); this selective Ca accumulation from soils with very low Ca:Mg ratios substantially reduces Mg and Ni toxicity (Kruckeberg 1991). Unless Ca is actually deficient, Ca addition has little effect on the Ni concentration in the above-ground biomass and shoot yield as well as root-to-shoot translocation of Ni, but may increase Ni tolerance (Chaney et al. 2008). Calcium supply in the form of CaCO₃ increases Ni uptake in hyperaccumulator plants growing on some soils, as a result of the combined effect of Ca addition and soil pH (Kukier et al. 2004). However, Ni tolerance in hyperaccumulator plants may be improved by CaSO₄ addition independent of soil pH (Chaney et al. 2008). Moreover, Ca is present in ultramafic soils at low concentrations; hence Ca depletion should be avoided in Ni phytomining operations (Bani et al. 2015a; Chaney et al. 2007b; Chaney et al. 2008). Apart from these observations, our current understanding about the role of Ca in hyperaccumulator plants is limited.

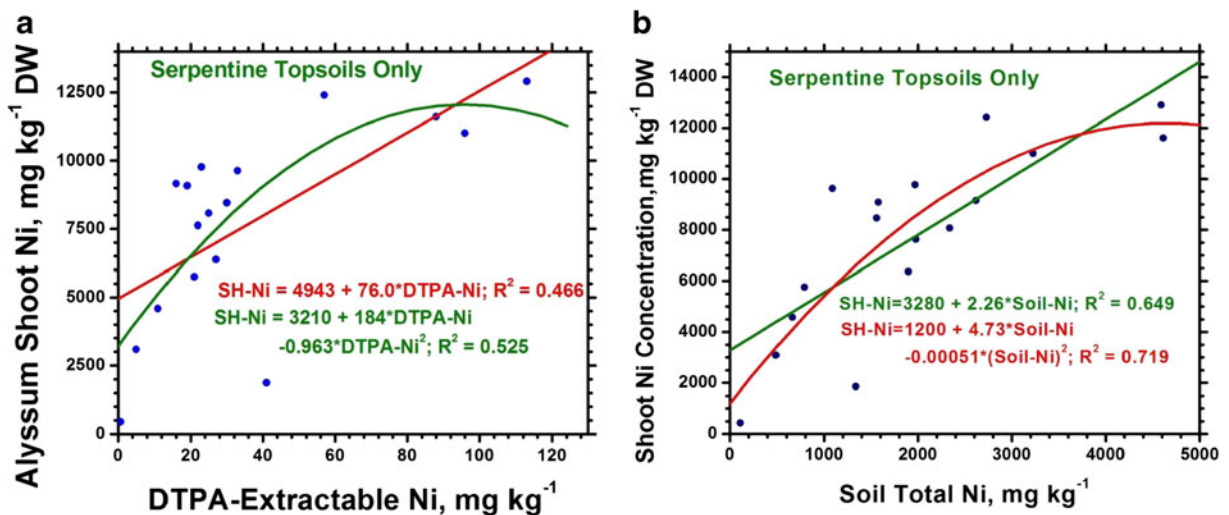


Fig 2 Relation of *Alyssum* shoot Ni to (a) DTPA-extractable Ni in 17 ultramafic topsoils; and (b) total soil Ni in 17 ultramafic topsoils

Soil S additions and Ni accumulation

Additions of soil S increase Ni yield in *B. coddii* but does not have a significant effect on biomass production (Robinson et al. 1999a). Sulphur additions in the form of elemental finely ground sulphur lower the soil pH, thereby increasing the NH_4 -acetate-extractable Ni fraction (Robinson et al. 1999b). However, limited studies exist on the use of S treatments in Ni phytomining (Table 2). Sulphur additions to ultramafic soils may enhance Ni uptake in Ni hyperaccumulator plants by increasing the extractability of Ni (Chaney et al. 2007a; Robinson et al. 1999a). Furthermore, S is reported to be taken up intensively by all Brassicaceae (i.e. *Alyssum* spp.) due to their specific metabolic requirements (e.g. in glucosinolates) (Booth et al. 1995) apart from any hyperaccumulation traits. Basic studies on Ni tolerance by *Noccaea* Ni hyperaccumulators (*Noccaea goesingense*, *N. oxyceras*, and *N. rosulare*) indicate that glutathione plays a role in Ni tolerance in these species (Freeman et al. 2004) and that a S-rich precursor of glutathione (L-cysteine) may be involved in Ni hyperaccumulation in *Noccaea* (Na and Salt 2011). Broadhurst et al. (2004b; 2009) reported co-localisation of Ni and S in vacuoles of *A. murale* and *A. corsicum* grown on ultramafic soils and in nutrient solutions and suggested SO_4^{2-} was needed as a counter-ion to maintain the charge balance in vacuoles storing high concentrations of Ni. Future studies need to assess the independent role of S on phytoavailability of Ni

in ultramafic soils, at least for Brassicaceae Ni hyperaccumulator plants.

Soil organic matter additions and Ni accumulation

The use of organic amendments in the culture of the Ni hyperaccumulators *Alyssum serpyllifolium* subsp. *lusitanicum*, *A. serpyllifolium* subsp. *malacitanum*, *A. bertolonii* and *N. goesingense* demonstrated substantial positive effects on the biomass yield of the plants (Álvarez-López et al. 2016). The authors found that the Ni yield was significantly increased due to the stimulation of biomass production while the organic amendments decreased both soil Ni availability and shoot Ni concentrations. The increase in biomass production could be due to improvements in the soil physical properties such as soil structure, porosity and water-holding capacity. Organic amendments could therefore be beneficial in Ni phytomining operations, but this need to be demonstrated in field trials.

Plant management practices

Nickel phytomining pot and field trials have shown that plant management practices, beyond fertiliser treatment and pH adjustment, may enhance Ni yield in Ni hyperaccumulators via a number of ways: (i) plant density is important to optimise biomass production per unit area (Bani et al. 2015b; Lasat 2002); (ii) weed control reduces competition for essential nutrients and water

between the ‘metal crop’ and weeds (Bani et al. 2015a; Chaney et al. 2007a); (iii) plant growth regulators may increase biomass production (Cabello-Conejo et al. 2014; Cassina et al. 2011) but can reduce their Ni yield (Cabello-Conejo et al. 2014), although a recent study shows positive effects on both biomass yield and Ni accumulation in two hyperaccumulator species (Durand et al. 2015); (iv) rhizobacteria may increase the phytoavailability of soil Ni (Abou-Shanab et al. 2006; Abou-Shanab et al. 2003) and (v) mycorrhizas may be critical for those hyperaccumulator species which are strongly associated by mycorrhizas, such as *B. coddii* (Orłowska et al. 2011).

In the only study to date that has used plant breeding techniques to produce improved ‘metal crop’ cultivars, Li et al. (2003b) showed a wide range of shoot Ni concentrations and yield of diverse *A. murale* and *A. corsicum* germplasm (Fig. 3). Using recurrent selection (required for self-incompatible species), the authors significantly increased shoot Ni concentration and yield of Ni during three cycles of selection. In this study, plant lines were also selected for retention of leaves during flowering so that the high Ni foliar biomass was not lost before harvest of the flowering crop. Collection of diverse germplasm followed by normal plant breeding techniques to improve the ‘metal crop’ is clearly a key step in developing the agronomy of phytomining.

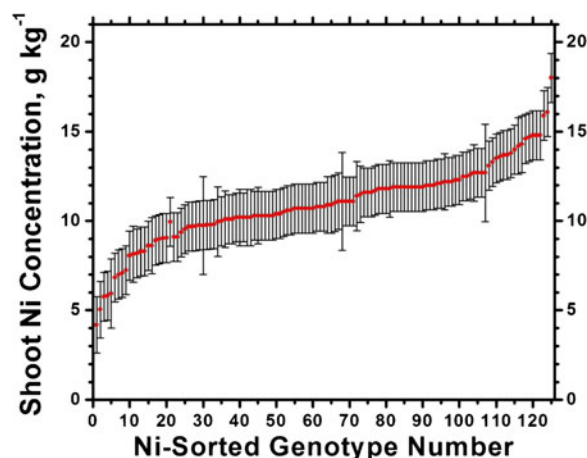


Fig 3 Variation in shoot Ni concentrations among *A. murale* genotypes grown to (mid-flowering) harvest stage on an Oregon Brockman variant ultramafic soil with 5500 mg kg⁻¹ Ni (Adapted with permission from Li et al. 2003b)

Soil physical properties

Soil physical properties influence Ni yield of hyperaccumulator plants, for example adequate soil drainage is an important factor in the agronomy of Ni phytomining. In a wet climate when soils are poorly drained, the growth of hyperaccumulator plants is adversely affected and plants may die before normal harvest time. Chaney et al. (2007a) have demonstrated in field trials that such conditions may be corrected by establishing plants with ridge tilling. Good soil water-holding capacity is also important for economic Ni phytomining. Soil moisture affects soil Ni extractability, Ni uptake by hyperaccumulator species, plant growth and ultimately Ni yield (Angle et al. 2003). *A. murale* and *B. coddii* grow well at high moisture content; Ni foliar concentration increases with increasing soil moisture content despite a decreasing trend in the soil Ni extractability (Angle et al. 2003). Addition of compost generally improves soil structure, porosity and water-holding capacity, and is likely beneficial for Ni phytomining operations.

Potential lifespan of profitable Ni phytomining operation

There is a time limitation for commercial Ni phytomining operations due to depleting soil Ni resources. To date, there have been no long-term repeated hyperaccumulator cropping experiments to ascertain the number of crop years that are possible for profitable Ni phytomining. We stress that an attempt to predict the lifespan via traditional soil extraction modelling may not be useful. From a five-year field trial, Bani et al. (2015a) suggested that economic Ni phytomining operations could be undertaken for at least several years (>10 years) before the need for soil modification (for example, ploughing). Many ultramafic soils contain >0.1 % total Ni concentrations and Ni yields of 200 and 110 kg ha⁻¹ could be achieved under intensive and extensive phytomining production systems, respectively. Considering 1 ha ultramafic substrate with total soil Ni 2000 µg g⁻¹ to a depth of 1 m, and assuming a bulk density of 1.5 kg L⁻¹, the resource contains about 30 t of Ni. Annual Ni yields of 200 and 110 kg ha⁻¹ on such a substrate only constitute 1/150 and 1.1/300, respectively of the total resource. If 10–20 % of the total soil Ni is available to plants over the time-scale of operations, profitable Ni phytomining of an intensive and extensive

systems could be sustainable over 15–30 years and 27–54 years, respectively.

The way ahead and challenges

Numerous Ni phytomining pot and field trials have been undertaken in Albania, Canada, France, Italy, New Zealand, Spain and USA. The Ni-rich soils that were used include ultramafic soils and Ni-contaminated soils. Studies have shown that soils with >0.1 % Ni and a large available soil Ni pool are suitable for Ni phytomining. Several Ni hyperaccumulator plants have been identified as suitable ‘metal crops’ of which *Alyssum* spp. and *B. coddii* have proven especially successful. Extensive soil and plant management practices have been tested for their effects on the Ni yield and biomass yield of the ‘metal crops’ (Table 2). Since the first field trial in California on a farmed ultramafic soil (USA), using *S. polygaloides* without fertiliser application, all other trials have

incorporated nutrient management. By way of conclusion, the agronomic trials undertaken to date have demonstrated that:

- i) N+P+K fertilisation, organic matter additions and plant growth regulators substantially increase the biomass yield of ‘metal crops’ without causing dilution in shoot Ni yields.
- ii) Soil pH adjustments, S additions, N fertilisation, and bacterial inoculation generally increase Ni phytoavailability, and consequently, Ni yield in ‘metal crops’.
- iii) Traditional chemical soil extractants used to estimate phytoavailability of trace elements are of limited use to predict Ni phytoavailability to ‘metal crop’ species and hence Ni uptake.
- iv) Calcium soil amendments are necessary during phytomining because substantial amounts of Ca are removed through harvesting of ‘bio-ore’. Future studies must provide information on the effect

Table 5 Major challenges and research priorities for developing Ni phytomining around the world

Steps to develop Ni phytomining	Challenges	Research priorities
Selection of Ni-rich soils	Phytoavailability of Ni in soils Topography/landform of sites Size of available land area Lease of land	Identify soils where Ni phytomining could be profitable. Develop Ni phytoavailability assays to predict Ni yield in metal crops. Negotiate land ownership agreements. Undertake repeated hyperaccumulator cropping experiments to assess the number of crop years possible for profitable phytomining.
Discovery and selection of ‘metal crops’	Native crops are most suitable requiring screening to happen at each locality Hypernickelophore species are very rare globally	There is the need for increased surveys especially in tropical regions. Breeding of improved cultivars to optimise growth rate and biomass production.
Soil and plant management practices	The Ni uptake and biomass yield of most potential phytomining ‘metal crops’ remain untested at scale	Greenhouse or growth chamber trials to assess Ni uptake and biomass yield of such crops. Test the effect of other plant management practices such as fertilization, crop rotation and mixed cropping on Ni yield.
Harvesting techniques	Different cropping systems may require different harvesting technique	Identify appropriate harvesting technique suitable for each cropping system.
Post-harvest processing of nickel	Nickel recovery using smelter is profitable, while other high value products such as pure Ni salts currently have limited markets	Explore more methods of producing high value Ni products with potential markets in the near future from the biomass ash. Explore the production of Ni catalysts from biomass.

- of Ca additions on labile Ni pools and Ni phytoavailability.
- v) Phosphorus fertilisation has a large effect on biomass yield of ‘metal crops’ when cultivated on ultramafic soils not previously fertilized with P.
 - vi) Additions of organic matter enhance soil physical properties; soil moisture has positive effects on soil Ni extractability, Ni uptake by hyperaccumulator species, plant growth and ultimately Ni yield.
 - vii) Repeated hyperaccumulator cropping may not only deplete soil phytoavailable Ni, but also promote transfer of non-labile soil Ni to phytoavailable forms.

Nickel phytomining has high economic potential, but large-scale demonstrations are needed to provide ‘real-life’ evidence for commercial operations (van der Ent et al. 2015a). Table 5 highlights the major challenges facing the commercial development and implementation of Ni phytomining, and presents the main research priorities.

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