Botanickel

By Aperam & Econick

Agromining – A European perspective

Antony van der Ent

econick

What are hyperaccumulators – the genetic material for agromining?

What are hyperaccumulators plants?

- Hyperaccumulators are plants that can accumulate metal(loid) elements at extremely high concentrations in their living shoots without suffering toxicity.
- A wide range of different elements can be hyperaccumulated, including Co, Cu, Tl, Se, Ce, Mn, Ni, Zn, *etc*.
- The definition is based on 2–3 orders of magnitude higher foliar concentrations than in normal plants growing on the same soils:

>100 mg kg^{-1} Cd, Se or Tl
>300 mg kg^{-1} Co or Cu
>1000 mg kg^{-1} Ni, As, REEs
>3000 mg kg^{-1} Zn
>10,000 mg kg^{-1} Mn

Extreme hyperaccumulation of nickel

- Some hyperaccumulators can reach up to 4 wt% Ni in their leaves and up to 25 wt% Ni in the sap.
- These are amongst the highest metal concentration in any living tissue, and it colors the sap literally green from Ni-ions.
- A mature tree can contain approximately 5 kilograms of Ni metal.

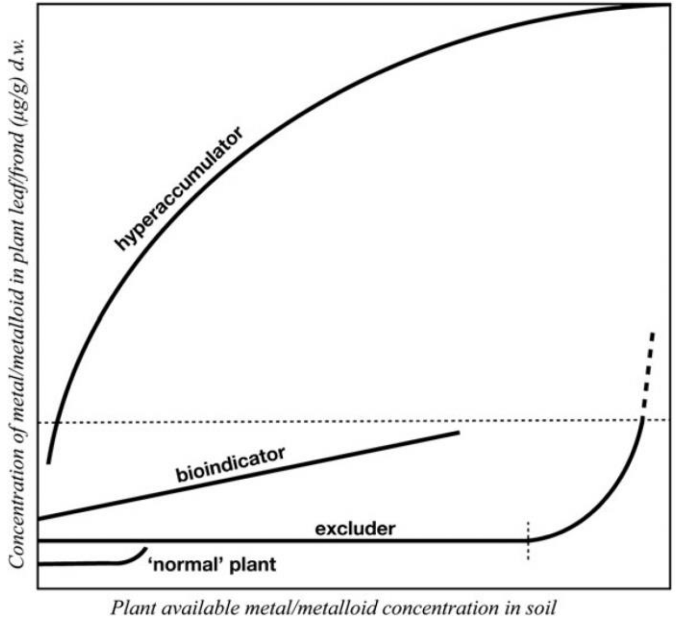
Source: https://pubs.acs.org/doi/10.1021/es506031u

The tree *Phyllanthus balgooyi* from Malaysia has 20 wt% Ni in phloem sap.

What are hyperaccumulator plants?

- The following criteria define a genuine hyperaccumulator species:

  i. Meets the foliar threshold concentration whilst growing on natural soil in nature
  ii. High shoot translocation (shoot to-root metal concentration quotient >1)
  iii. Has extreme level of metal tolerance (‘hypertolerance’)
  iv. Non-linear response to soil metal with Bioconcentration Factor >1 (often >50)
  v. Completes the life cycle from seed to seed whilst hyperaccumulating



Source: https://link.springer.com/article/10.1007/s11104-012-1287-3

Common misconceptions & caveats

- Plants grown on hydroponics alone cannot be used to establish hyperaccumulation status, this must (also) be tested on soils or substrates.

- Nominal threshold concentrations are not sacrosanct and should be used sensibly. For example, a plant with 999 mg kg^{-1} *vs*. 1001 mg kg^{-1} foliar Ni.

- The most important trait for successful agromining is a foliar concentration >10,000 mg kg^{-1} (>1 wt%) for 'medium value' elements **Ni, Mn, Zn** and lower (>0.1 wt%) for 'high value' elements **Se, Tl, REEs**.

Plant Soil
DOI 10.1007/s11104-012-1287-3

REGULAR ARTICLE

Hyperaccumulators of metal and metalloid trace elements: Facts and fiction

Antony van der Ent · Alan J. M. Baker ·
Roger D. Reeves · A. Joseph Pollard · Henk Schat

Common misconceptions & caveats

- The Bioconcentration Factor cannot be used to establish whether a species is a hyperaccumulator, for example: 10 mg kg^{-1} metal in the soil and 20 mg kg^{-1} in the root/shoot = BCF >1, but <u>not</u> a hyperaccumulator!

- Genuine hyperaccumulation: *Noccaea caerulescens* with >20,000 mg kg^{-1} Zn in the shoot when growing in soil <100 mg kg^{-1} Zn.

- No known graminoid/grass or aquatic macrophyte species meets the criteria for a hyperaccumulator. Hyperaccumulation status of algae is unknown.

Are Grasses Really Useful for the Phytoremediation of Potentially Toxic Trace Elements? A Review

Flávio Henrique Silveira Rabêlo[1], Jaco Vangronsveld[2,3], Alan J. M. Baker[4,5,6], Antony van der Ent[4] and Luís Reynaldo Ferracciú Alleoni[1]*

[1] Luiz de Queiroz College of Agriculture, University of São Paulo, Piracicaba, Brazil, [2] Centre for Environmental Sciences, Hasselt University, Diepenbeek, Belgium, [3] Department of Plant Physiology and Biophysics, Maria Curie-Skłodowska University, Lublin, Poland, [4] Centre for Mined Land Rehabilitation, Sustainable Minerals Institute, The University of Queensland, Brisbane, QLD, Australia, [5] School of BioSciences, The University of Melbourne, Parkville, VIC, Australia, [6] Laboratoire Sols et Environnement, Université de Lorraine – INRAE, Nancy, France

How many hyperaccumulators are there?

- To date, 721 hyperaccumulators have been identified globally (out of >350,000 known plant species), although many more likely await discovery.

- These are from 52 families and130 genera – families most strongly represented are Brassicaceae (83 species) and Phyllanthaceae (59 species).

Element	Threshold (μg g^{-1})	Families	Genera	Species	Global records
Arsenic (As)	> 1000	1	2	5	*Pteris vittata*[1] (2.3%)
Cadmium (Cd)	> 100	6	7	7	*Arabidopsis halleri*[2] (0.36%)
Copper (Cu)	> 300	20	43	53	*Aeolanthus biformifolius*[3] (1.4%)
Cobalt (Co)	> 300	18	34	42	*Haumaniastrum robertii*[4] (1%)
Manganese (Mn)	> 10 000	16	24	42	*Virotia neurophylla*[5] (5.5%)
Nickel (Ni)	> 1000	52	130	532	*Berkheya coddii*[6] (7.6%)
Lead (Pb)	> 1000	6	8	8	*Noccaea rotondifolia* subsp. cepaeifolia[7] (0.8%)
Rare earth elements (lanthanum, La; cerium, Ce)	> 1000	2	2	2	*Dicranopteris linearis*[8] (0.7%)
Selenium (Se)	> 100	7	15	41	*Astragalus bisulcatus*[9] (1.5%)
Thallium (Tl)	> 100	1	2	2	*Biscutella laevigata*[10] (1.9%)
Zinc (Zn)	> 3000	9	12	20	*Noccaea caerulescens*[11] (5.4%)

Source: https://nph.onlinelibrary.wiley.com/doi/10.1111/nph.14907

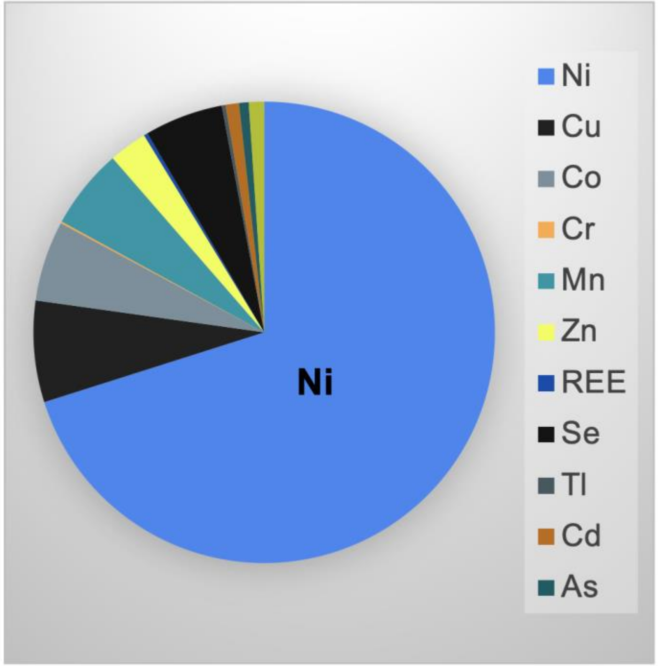
Where do hyperaccumulators occur?

- Nickel hyperaccumulators make up the greatest number of hyperaccumulators globally (approx. 500 out of 700+ species).

- This reflects the fact that worldwide surface exposures of naturally Ni ultramafic soils cover >3% of the Earth's surface.

- Most Ni hyperaccumulator species have been documented in the following countries:

    - Cuba (130 species)
    - New Caledonia (65 species)
    - Turkey (59 species)
    - Brazil 30 (species)
    - Malaysia (28 species)



Periodic Table of Hyperaccumulation

Source: https://pubs.rsc.org/en/content/articlelanding/2020/mt/c9mt00263d

Cu-Co hyperaccumulator *Haumaniastrum katangense* from the DR Congo

Se hyperaccumulator *Neptunia amplexicaulis* from Australia

Zn-Cd hyperaccumulator *Noccaea caerulescens* from Europe

Zn-Cd hyperaccumulator *Sedum plumbizincola* from China

Tl hyperaccumulator *Biscutella laevigata* from France

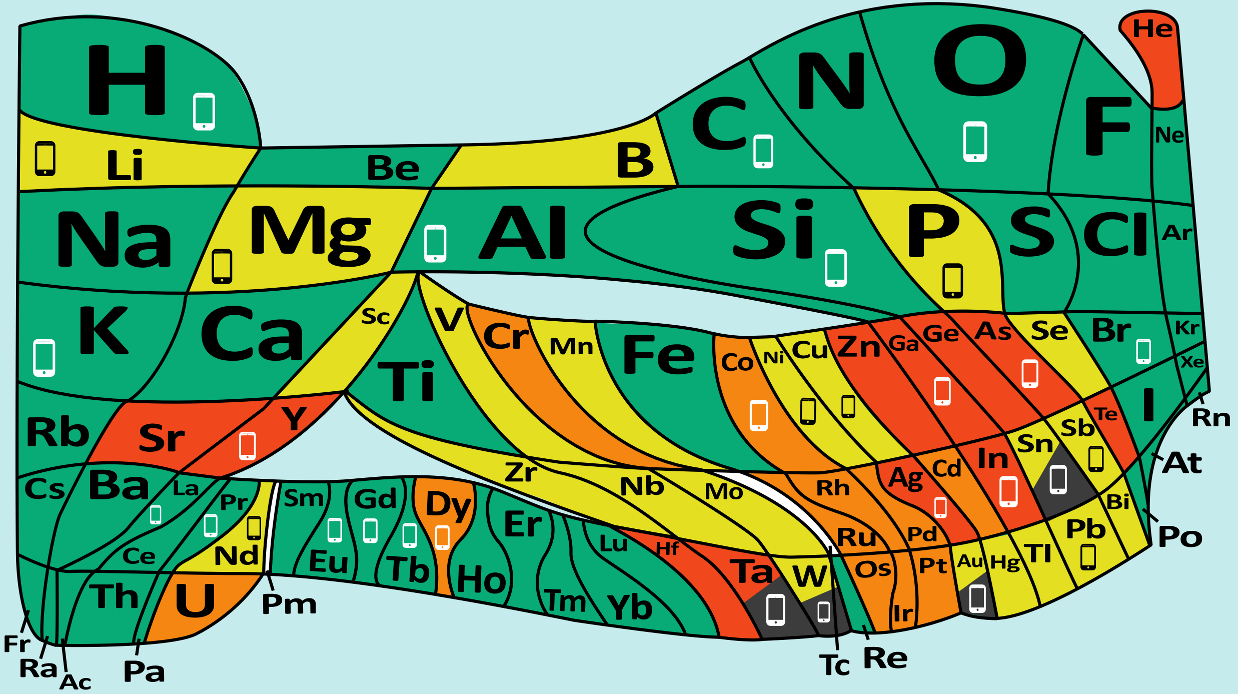
Ni hyperaccumulator *Odontarrhena chalcidica* from Europe

United Nations
Educational, Scientific and
Cultural Organization

2019 IYPT
International Year
of the Periodic Table
of Chemical Elements

The 90 natural elements that make up everything

How much is there? Is that enough?



Serious threat in the next 100 years

Rising threat from increased use

Limited availability, future risk to supply

Plentiful Supply

Synthetic

From conflict minerals

Elements used in a smart phone

Inspired by WF Sheehan's 'A Periodic Table with Emphasis' published in Chemistry, 1976, 49, 17-18'

Read more and play the video game **http://bit.ly/euchems-pt**

EuChemS
European Chemical Society

Developing agromining – some considerations

What is agromining (or metal farming)?

- Agromining uses hyperaccumulator plants to take up metal in biomass.

- Harvesting and (pyro/hydro-metallurgical) processing of the biomass generates a high-grade bio-ore.

- Agromining may in principle be undertaken to produce Se, Cd, Co, REEs, Mn, Ni, Tl, and Zn, as hyperaccumulator plants are known for these elements.

- However, Cu and Pb hyperaccumulators have poor accumulation characteristics and are therefore not suitable for agromining.

What kinds of agromining may be economical?

- Current market prices per metric ton are high for:
  - Ni (US$21,000)
  - Se (US$52,000)
  - Tl (US$60,000)
  - REEs (US$10,000 on REO basis)
- …. but market prices are much lower for:
  - Mn (US $2350)
  - Zn (US$2100)

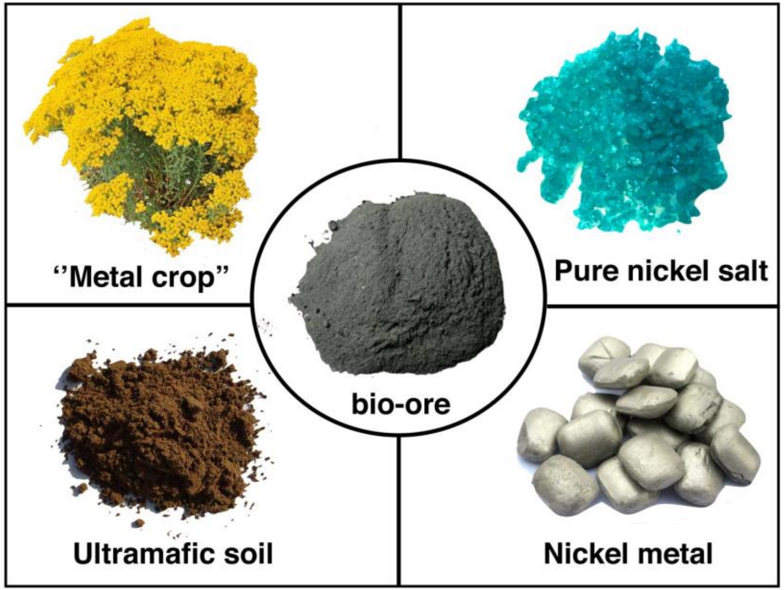
- Agromining may therefore be feasible for **Ni, Se, Tl**, but of these elements, large surface areas with natural geogenic enrichment exist only for **Ni** and **Se**.

- Only for **Ni** is there a sufficiently large global market for industrial off-take of agromined product.

- Price volatility in REE prices and new R&D efforts could enable REE agromining.

What is agromining (or metal farming)?

- Ultramafic soils have developed over ultramafic rocks which are naturally enriched in Ni (usually 0.2–1 wt% Ni).
- These are abundant all around the world, especially in the Mediterranean region.
- Ultramafic soils are very infertile and unsuitable for conventional agriculture of food crops… but can be agromined!
- Strip-mined land in conventional Ni mining as well as mine wastes sites (‘second mining’) are potential targets for agromining too.



Source: https://pubs.acs.org/doi/10.1021/es506031u

Mined or degraded Ni-rich land

Low productive ultramafic land

Source: https://pubs.acs.org/doi/10.1021/es506031u

Integrated in rehabilitation strategy

Improving soil fertility on agricultural land

Agromining operations

- Key ‘metal crops’ in temperate and Mediterranean climate regions include *Odontarrhena chalcidica* (formerly *Alyssum murale)* and other species of the genus *Odontarrhena*.

- *Odontarrhena chalcidica* is a biannual species that requires re-sowing every other year.

- Sustained yield over 20–30 years of 150–250 kg of nickel-metal per hectare per year for *Odontarrhena* spp.

- At the base nickel value of $15 kg (5-year average price), this is worth $2250–3750 per hectare per year (excluding production and processing costs of bio-ore).

Life time of an agromining operation

- The commercial returns from an agromining venture will be finite due to the diminishing concentrations of the target metal in the substrate.

- For 1 ha with total Ni with 2000 mg kg^{-1} to a depth of 1 m, this is 30 t of contained Ni. Crops with 5 t ha^{-1} at 2 wt% Ni yield 100 kg Ni ha^{-1}.

- If 10−20% of the total amount of soil Ni is part of the plant available-pool, the agromining operation could be sustainable over at least 30 years.

- Compared to conventional mining, the time to first production is much shorter for agromining and the average life of a conventional Ni mine also suffers from degrading ores over time.

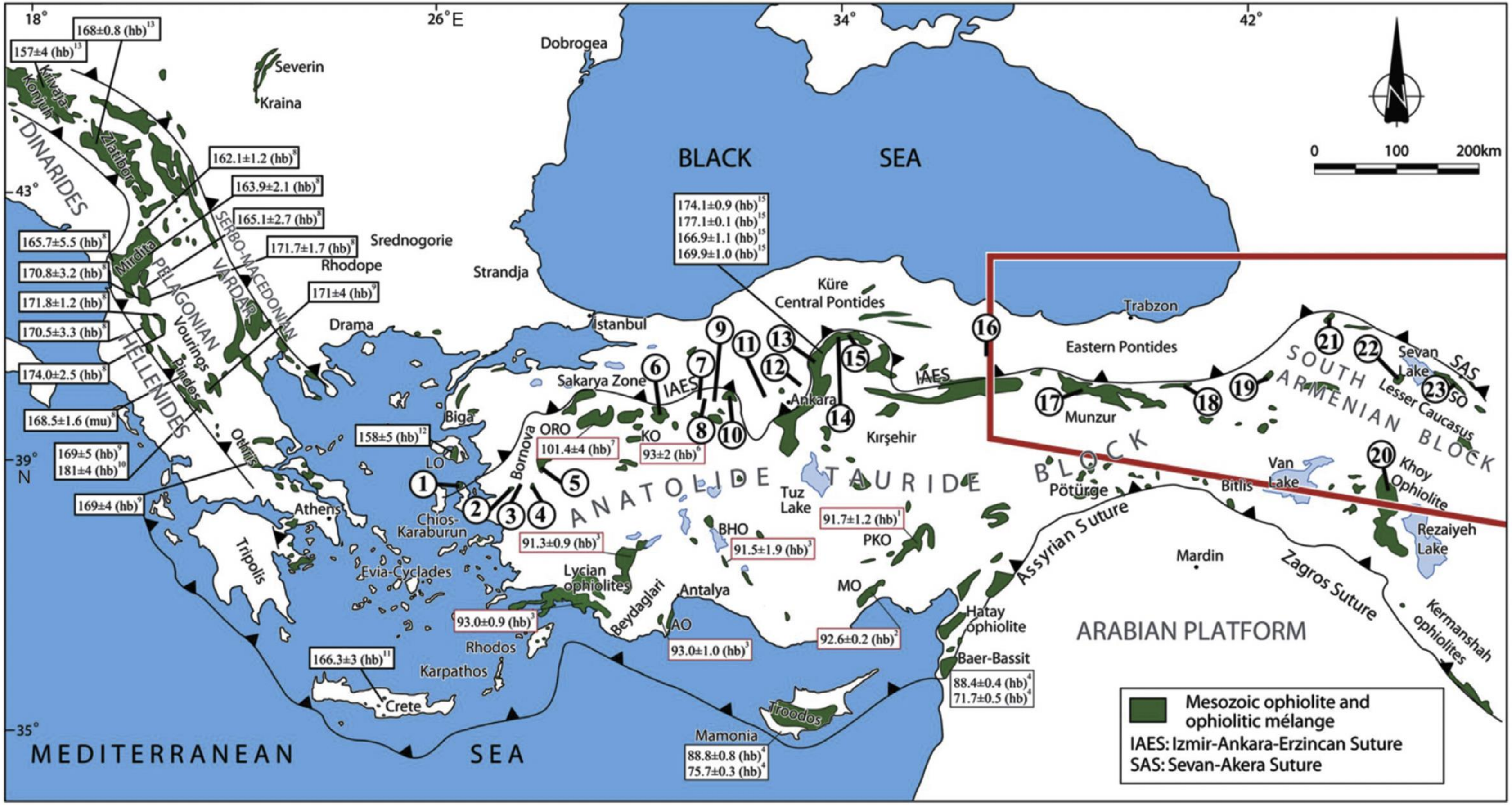
Target areas and metal crop criteria

Target areas for nickel agromining

- Not all areas and types of ultramafic soils are suitable for agromining.

- Some of the key factors to consider for site selection include:

i. Occurrence of >100 km^2 contiguous ultramafic soil to establish a local industry
ii. Ferralsols common in the tropics are <u>not</u> useable for agromining
iii. Ultramafic soils >2000 mg kg^{-1} total Ni and >200 mg kg^{-1} DTPA-extractable Ni
iv. Suitable <u>native</u> hyperaccumulator species are available
v. Soils capable of being easily cropped with local agricultural methods
vi. Local infrastructure and 'social license to operate' are important



Source: Geodinamica Acta 26(3-4):311-330. DOI:10.1080/09853111.2013.877236

Target areas for nickel agromining

- Extensive field trials have been conducted across Europe, first in Albania and as part of the EU-funded LIFE AGROMINE Project in Spain, Greece and Austria.

- The field trials involved *Odontarrhena* species and established agronomic practises, including sowing, optimum density, fertilisation, harvesting, *etc*.

- Post-harvesting processing of the bio-ore, including extensive hydrometallurgical process routes, were developed.

- Life Cycle Assessments and Techno-Economical Assessments were performed for Ni agromining in the European context.

Main metal crop in Mediterranean climate are species of *Odontarrhena* that are cultivated in annual cycles. Each crop is 20 metric tonnes biomass hectare/year yielding up to 300 kg nickel metal.

Target criteria for nickel metal crops

- Only hyperaccumulator species that can accumulate >1 wt% (10,000 mg kg^{-1}) of of Ni in dry shoot biomass are suitable.

- Target is an annual yield of >80 kg Ni/ha/year (optimum >200 kg Ni/ha/year)

- Desirable properties include fast growth rates, easy mass propagation, high biomass production and adaptation to local edaphic and climate conditions.

- Where the climate does not change drastically from one season to another, perennial hyperaccumulator plants do not need to be re-sown on an annual basis.

What is agromining (or metal farming)?

- *Odontarrhena* are naturally dominant 'weeds' of agricultural fields on ultramafic soils in the Mediterranean Region, especially across the Balkans.

- At least 30 taxa of *Odontarrhena* are Ni hyperaccumulators.

- However, the genus *Odontarrhena* (*Alyssum*) is by no means the only with suitable metal crops, others include *Bornmuellera/Leptoplax, Noccaea, etc.*

- Other species from Mediterranean-type climate may also be used, such as *Berkheya coddii* from South Africa.

Nickel hyperaccumulator *Odontarrhena chalcidica* from the Mediterranean region

Nickel hyperaccumulator *Berkheya coddii* from South Africa

Target criteria for nickel metal crops

- Even though >500 Ni hyperaccumulator species are now known globally, very few meet the essential criteria for use a metal crop.
- Currently, at the most 50 ‘hypernickelophores’ (hyperaccumulators >1 wt% Ni) with sufficient biomass yield are globally part of the agromining toolkit.
- The metal crop species to be used should always be carefully; matched to the local climatic and edaphic conditions.
- Preferably local native species are used in any agromining operation.

Discovery of novel hyperaccumulator plants

Discovery of hyperaccumulators

- Although numerous Ni hyperaccumulator plant species are known, the hunt is out to discover the next target metal crop species with just the right characteristics for agromining.

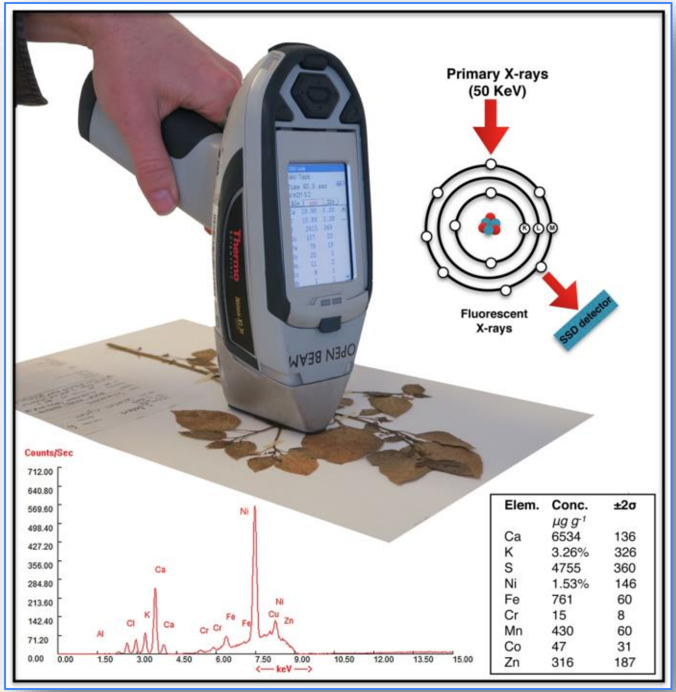
- In particular, perennial species with high biomass are desirable. Other optimal traits include drought/heat and pest resistance.

- Herbaria represent the greatest repositories of biological information in the world.

- Portable X-ray Fluorescence (XRF) spectroscopy is a time- and cost-effective method to measure elemental concentrations in herbarium specimens.

Global herbaria for hyperaccumulator discovery

- Elements such as Ni, Mn, Co, Zn in herbarium specimens can be measured with XRF at a rate of 300 specimens/day (translating to 6000 specimens/month).
- Herbarium XRF surveying is game-changing for the discovery of new hyperaccumulators.
- Highly probable that numerous hyperaccumulators, including new metal crops with desirable characteristics, will be discovered in this way.



Source: https://www.nature.com/articles/s41598-019-40050-6

Conclusions and outlook

R&D directions for Ni agromining

- To date, no specific crop breeding and improvement has taken place on any metal crop, but there is tremendous potential for advanced breeding programmes to dramatically improve the attainable Ni yield.

- There is scope for at least a two-fold improvement of Ni yield in *Odontarrhena* based on genotypic variability in shoot Ni accumulation.

- Nickel transport pathways in hyperaccumulator plants have not yet been identified, but if known offer tangible options for genetic improvement, for example by over-expressing Ni transporters in the roots.

Rare Earth Element (REE) hyperaccumulation & potential for REE agromining

Rare Earth Element hyperaccumulation

- Rare Earth Elements (REEs) have no physiological role and no plant takes REE up specifically – uptake and translocation *via* Al/Si-pathways.

- REE hyperaccumulation is principally known from the tropical fern *Dicranopteris linearis* from China with up to 7000 mg kg^{-1} REEs.

- In the USA, trees of the genus *Carya* (Juglandaceae) with *C. tomentosa* and *C. glabra* with a remarkable ability to accumulate REEs up to 2300 mg kg^{-1}… but they are all very slow growing.

- *Phytolacca americana* (Phytolaccaceae) can also accumulate REEs with up to 1040 mg kg^{-1} …. but are fast-growing and have high biomass.

Rare Earth Element hyperaccumulation

- Areas with surface outcropping geogenic REE-enrichment (100–1000s mg kg^{-1}), are abundant around the world, for example, rhyolites at Trans-Pecos, Texas.

- Depending on the specific mineralogy (*e.g.*, easily weatherable phases – bastnäsite), some of these deposits have highly plant-available REEs.

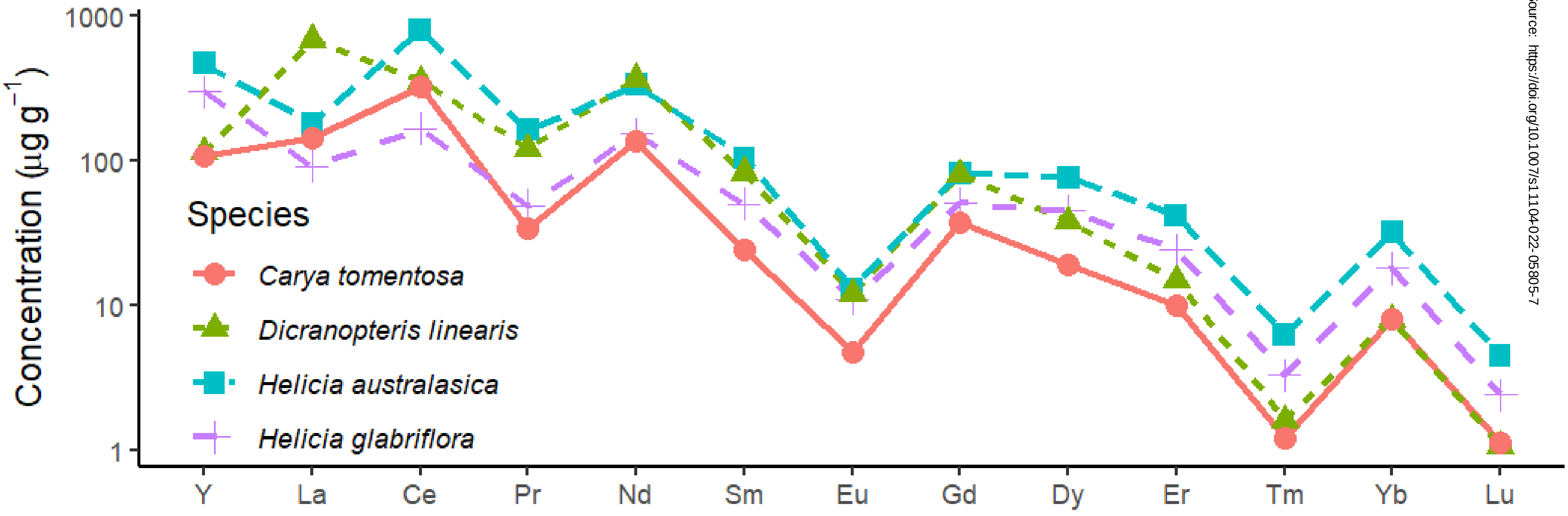
- Plants with carboxylate-exuding cluster roots, such as *Phytolacca* spp. can lixiviate REEs from soil mineral phases.

- Potential for REE agromining is likely very substrate-specific and needs to be tested under realistic conditions (not hydroponics).

Phytolacca americana grown on REE-enriched tailings accumulating up to 3000 mg kg^{-1} REEs.

Helicia glabriflora growing naturally on a soil with 60 mg kg^{-1} REEs and accumulating up to 965 mg kg^{-1} REEs.

Source: https://doi.org/10.1007/s11104-022-05805-7



Source: https://doi.org/10.1007/s11104-022-05805-7

Rare earth elements (REE) concentrations of *Helicia australasica* and *H. glabriflora* (determined by ICP-AES) and the well-known REE (hyper)accumulator plant species *Carya tomentosa* (Wood and Grauke 2011) and Dicranopteris linearis (Liu et al. 2020).

https://nos.nl/

Botanickel
By Aperam & Econick

Our Vision | Our Approach | About the Joint Venture | Our Commitments | Contact | en

The Power of the Plant

Using plants to extract nickel from soil and then turning that nickel into stainless steel may sound like science fiction, but that's exactly what Botanickel is doing.

Read more

Botanickel
By Aperam & Econick

Our Approach

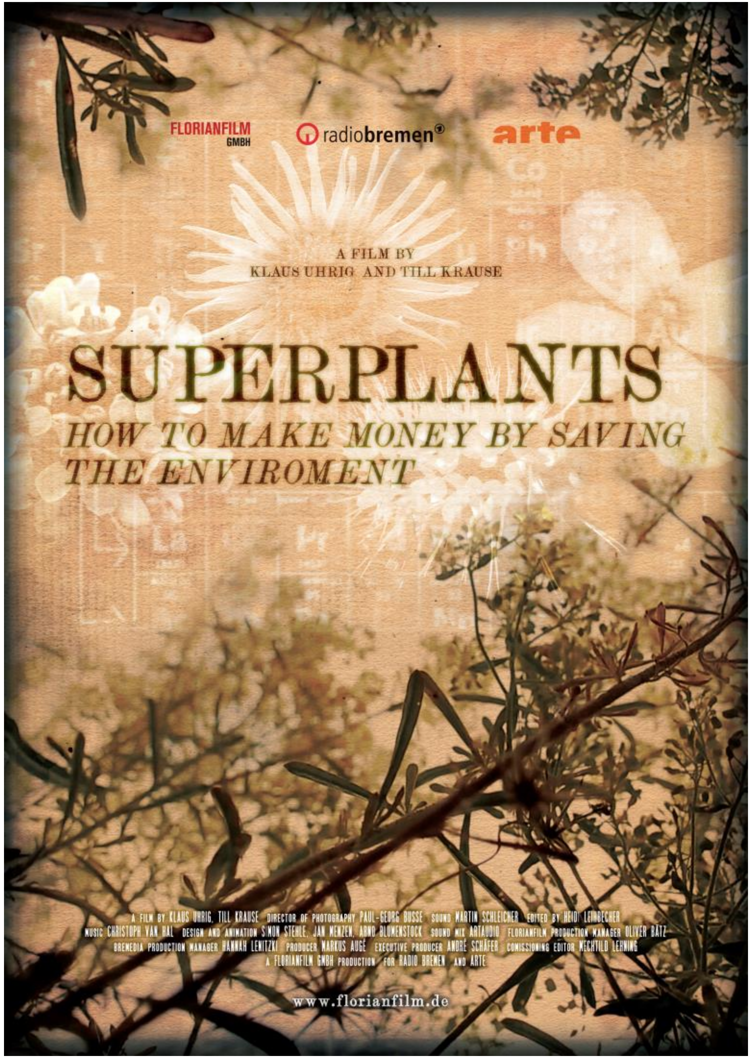
Bio-Sourced Nickel Done Right

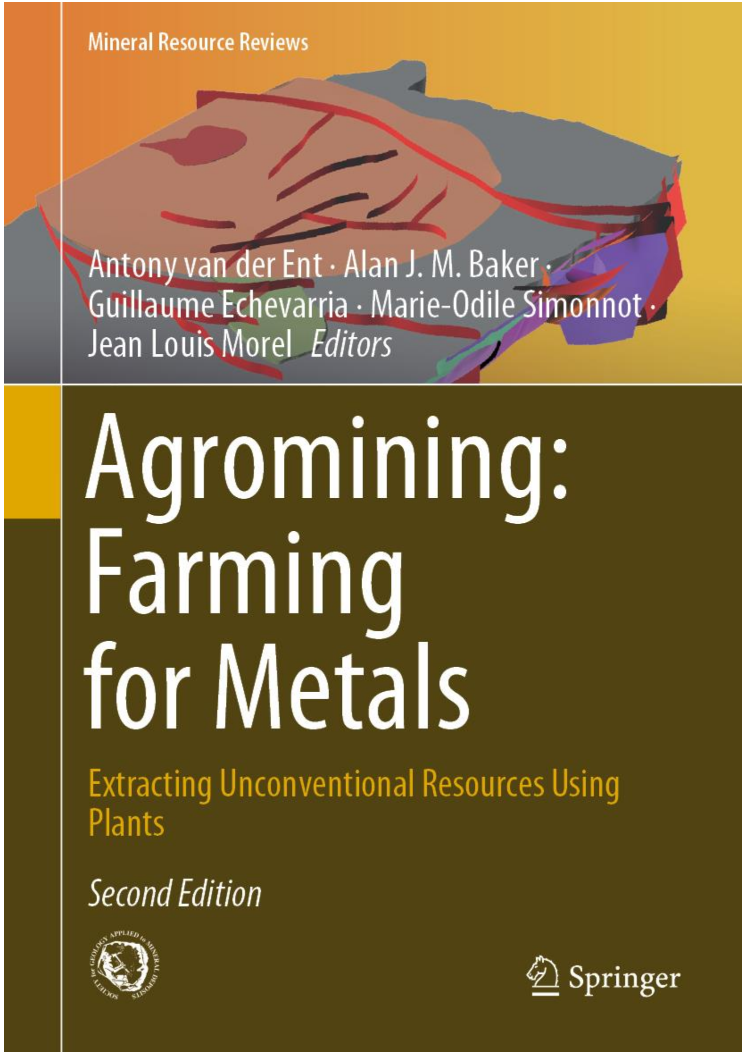
Botanickel's activity is designed to meet the needs and challenges of a world well-aware of the **limits of its planetary resources**, around a value chain that is innovative, is environmentally friendly and creates shared values over the long-term.

- Remediation and improvement of land with low agricultural yields due to the presence of nickel
- Production of renewable energy from the harvested biomass
- Recovery and upgrading of extracted nickel for use in the production of stainless steel
- Production of bio-based fertilisers

The development and deployment of this activity will be carried out in close collaboration with local populations and communities.

A value chain adapted to the local context, needs, and constraints..


FLORIANFILM GMBH
radiobremen
arte
A FILM BY
KLAUS UHRIG AND TILL KRAUSE
SUPERPLANTS
HOW TO MAKE MONEY BY SAVING THE ENVIROMENT
A FILM BY KLAUS UHRIG, TILL KRAUSE DIRECTOR OF PHOTOGRAPHY PAUL-GEORG BUSSE SOUND MARTIN SCHLEICHER EDITED BY HEIDI LEINBECHER
MUSIC CHRISTOPH VAN HAL DESIGN AND ANIMATION SIMON STEHLE, JAN MENZEN, ARND BLUMENSTOCK SOUND MIX ARTAUDIO FLORIANFILM PRODUCTION MANAGER OLIVER BÄTZ
BREMEDIA PRODUCTION MANAGER HANNAH LENITZKI PRODUCER MARKUS AUGÉ EXECUTIVE PRODUCER ANDRÉ SCHÄFER COMISSIONING EDITOR MECHTILD LEHNING
A FLORIANFILM GMBH PRODUCTION FOR RADIO BREMEN AND ARTE
www.florianfilm.de


Mineral Resource Reviews
Antony van der Ent · Alan J. M. Baker · Guillaume Echevarria · Marie-Odile Simonnot · Jean Louis Morel Editors
Agromining: Farming for Metals
Extracting Unconventional Resources Using Plants
Second Edition
Springer