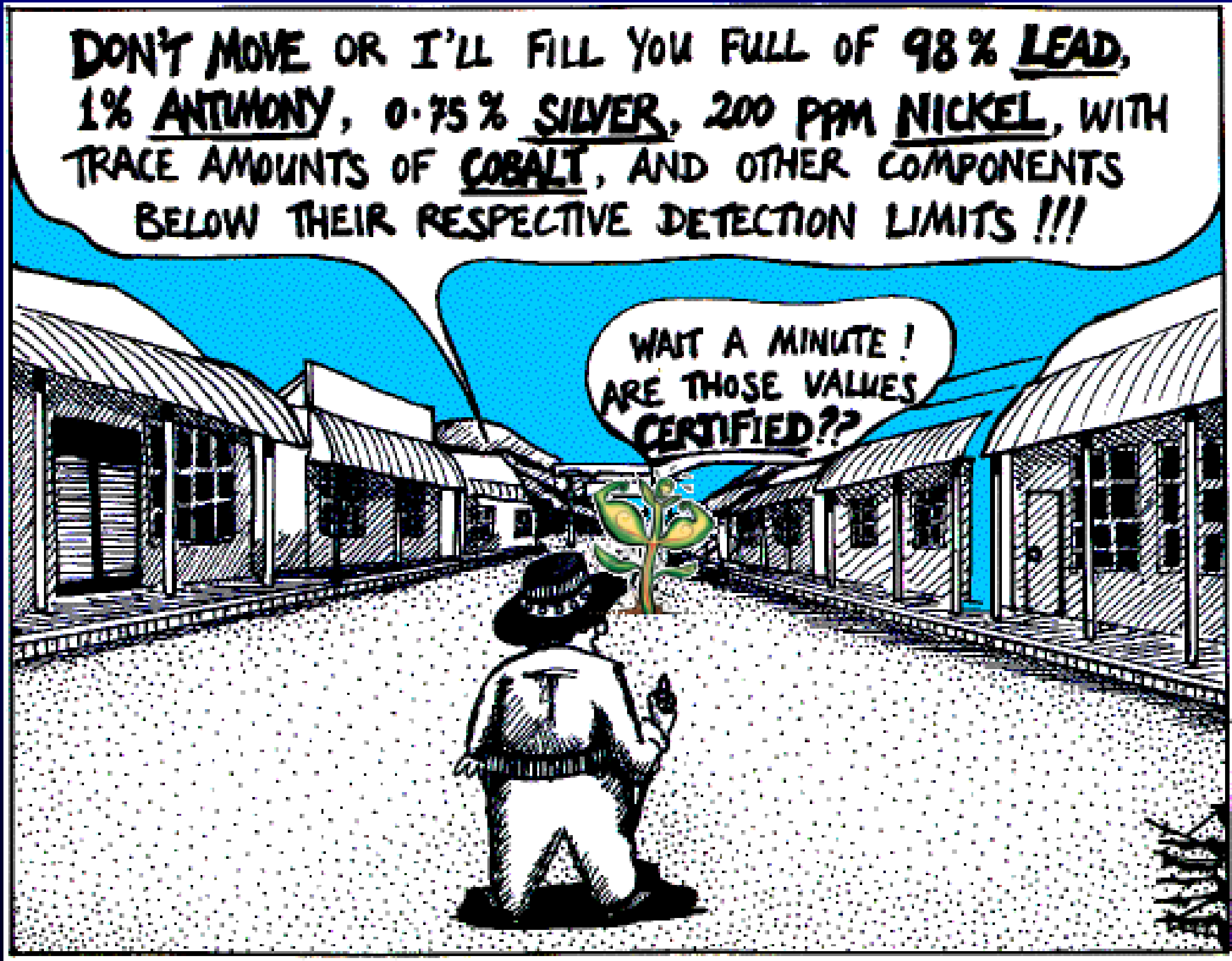
Heavy Metals and Plants - a complicated relationship
→ Biotechnological use of heavy metal accumulation in plants

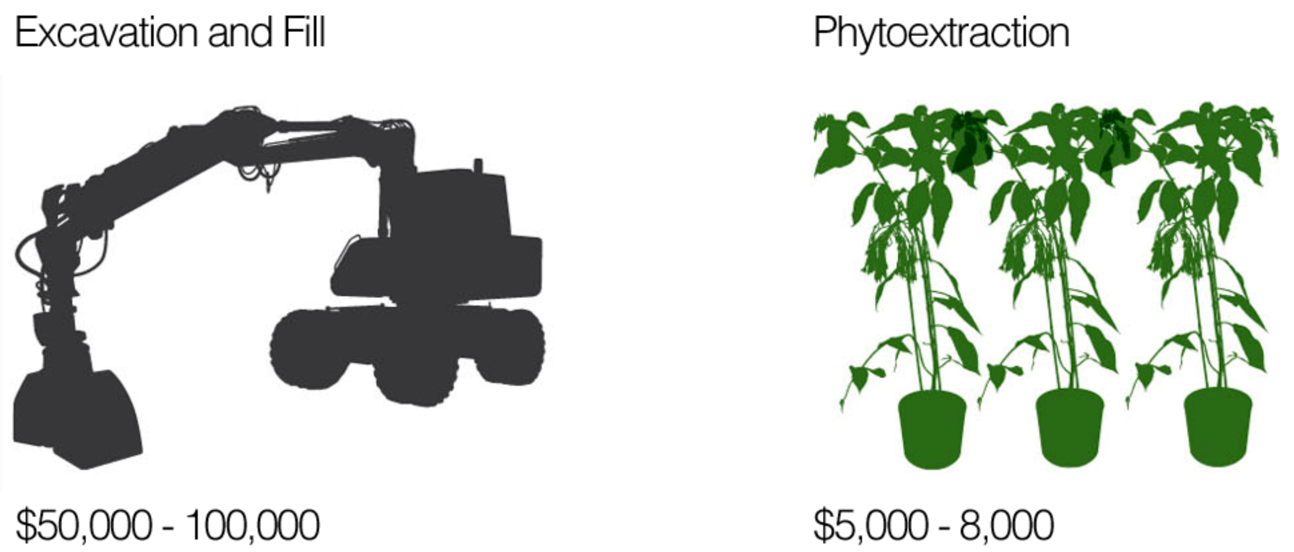


Heavy metal-hyperaccumulation in the Wild West

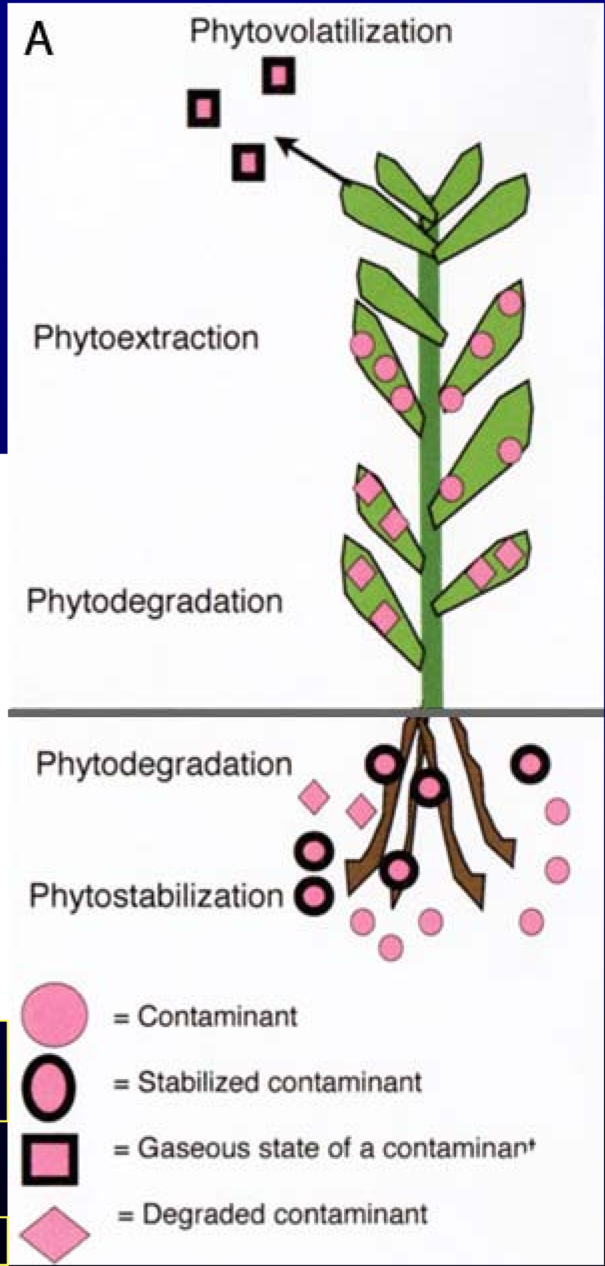
modified from: http://strangematter.sci.waikato.ac.nz/

Why phytoremediation?

- Low-cost method: soil does not have to be removed
- In some cases, metals may be recovered
- Final removal of pollution possible (in contrast to covering up polluted sites as done earlier)

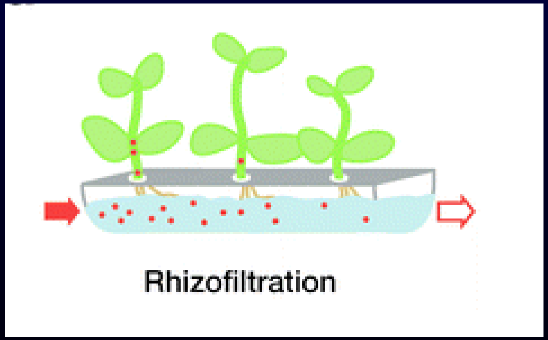


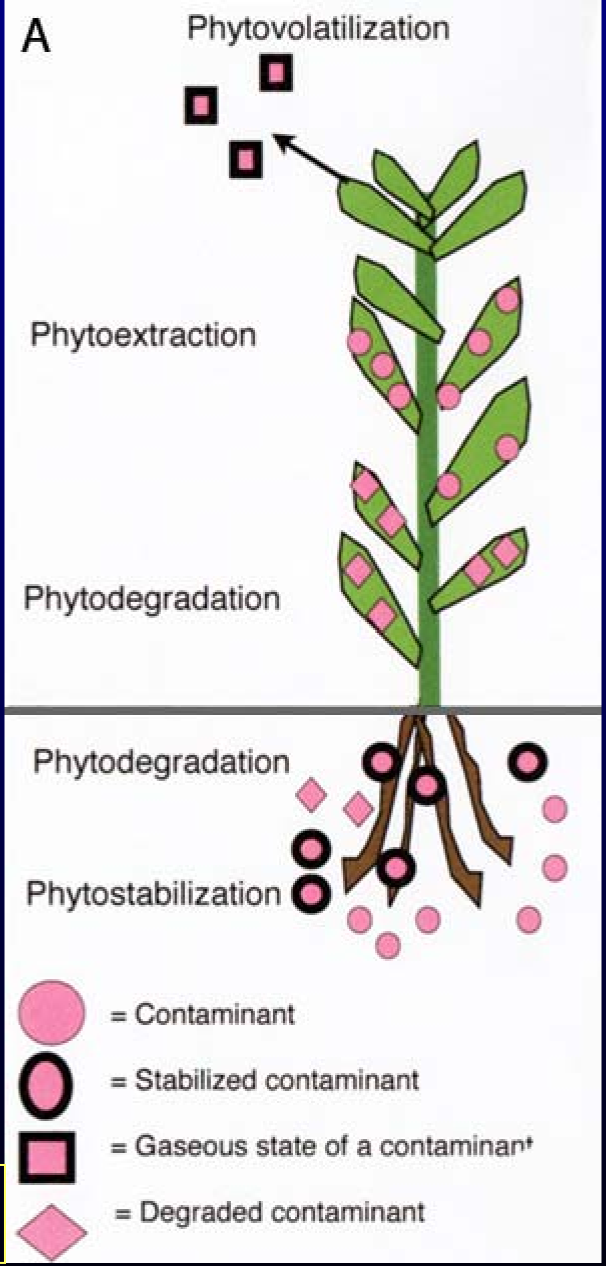
from: http://urbanomnibus.net/2010/11/from-brownfields-to-greenfields-a-field-guide-to-phytoremediation/



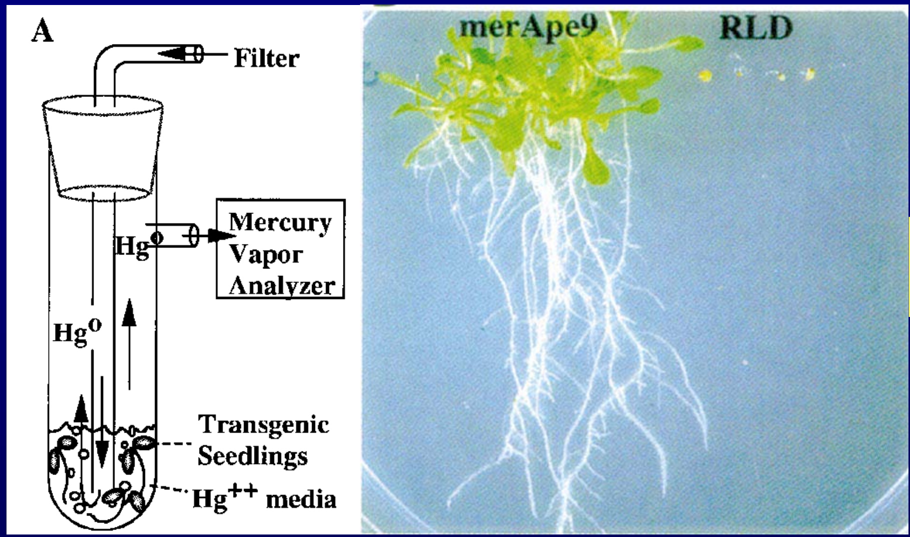
Types of phytoremediation

- Phytoextraction: removal of toxic substances by uptake usually into shoots
- Rhizofiltration: removal of toxic substances from water by adhesion to roots of swamp plants)
- Phytostabilisation: prevention of metal leakage from contaminated soils
- Phytodegradation: detoxification of pollutants by metabolisation in plants
- Phytovolatilisation: re-distribution of pollutants by transformation into volatile forms





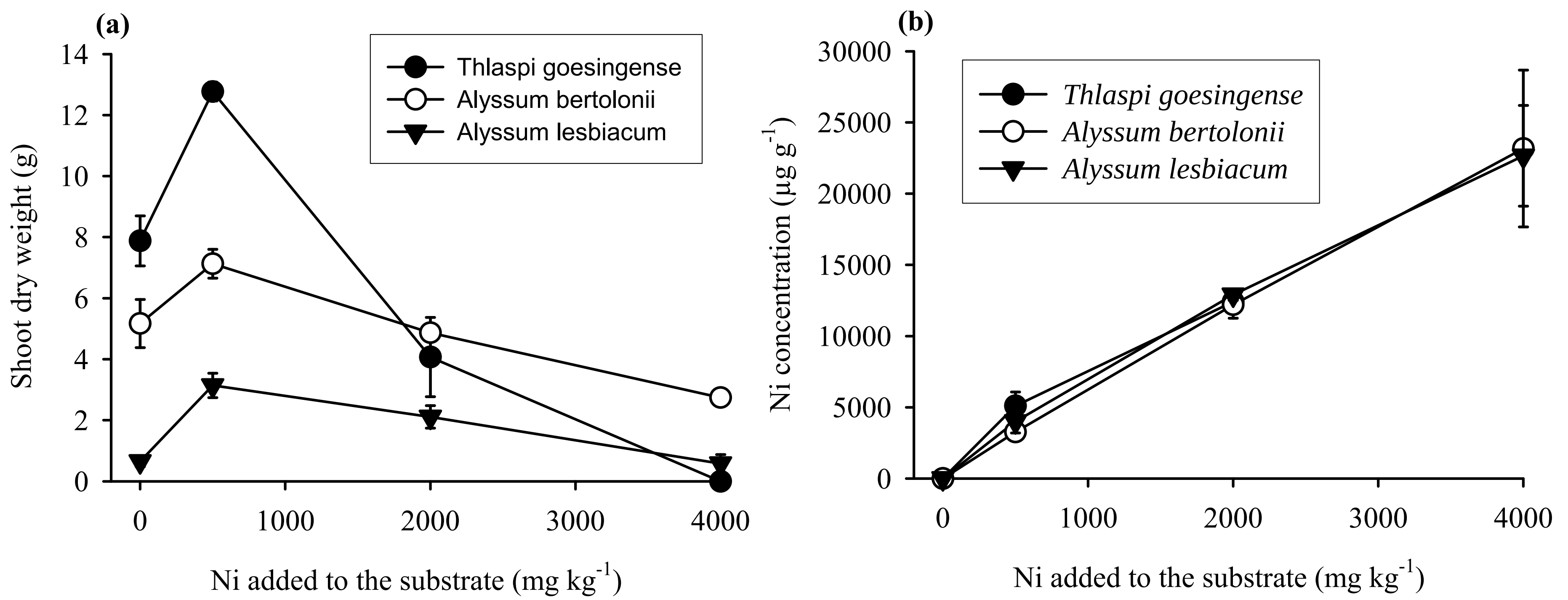
Mercury volatilisation by transgenic plants



Rugh CL, et al, 1996, PNAS 93, 3182-3187

• Reduction by reductases, e.g. Hg^{2+} --> Hg_0, Cu^{2+} --> Cu^+

Plants with an unusual appetite: Heavy metal hyperaccumulation



Effects of Ni^{2+} addition on hyperaccumulator plant growth and Ni^{2+} concentration in shoots

Küpper H, Lombi E, Zhao FJ, Wieshammer G, McGrath SP (2001) J Exp Bot 52 (365), 2291-2300

Cadmium deficiency in the Cd/Zn hyperaccumulator *Thlaspi caerulescens*

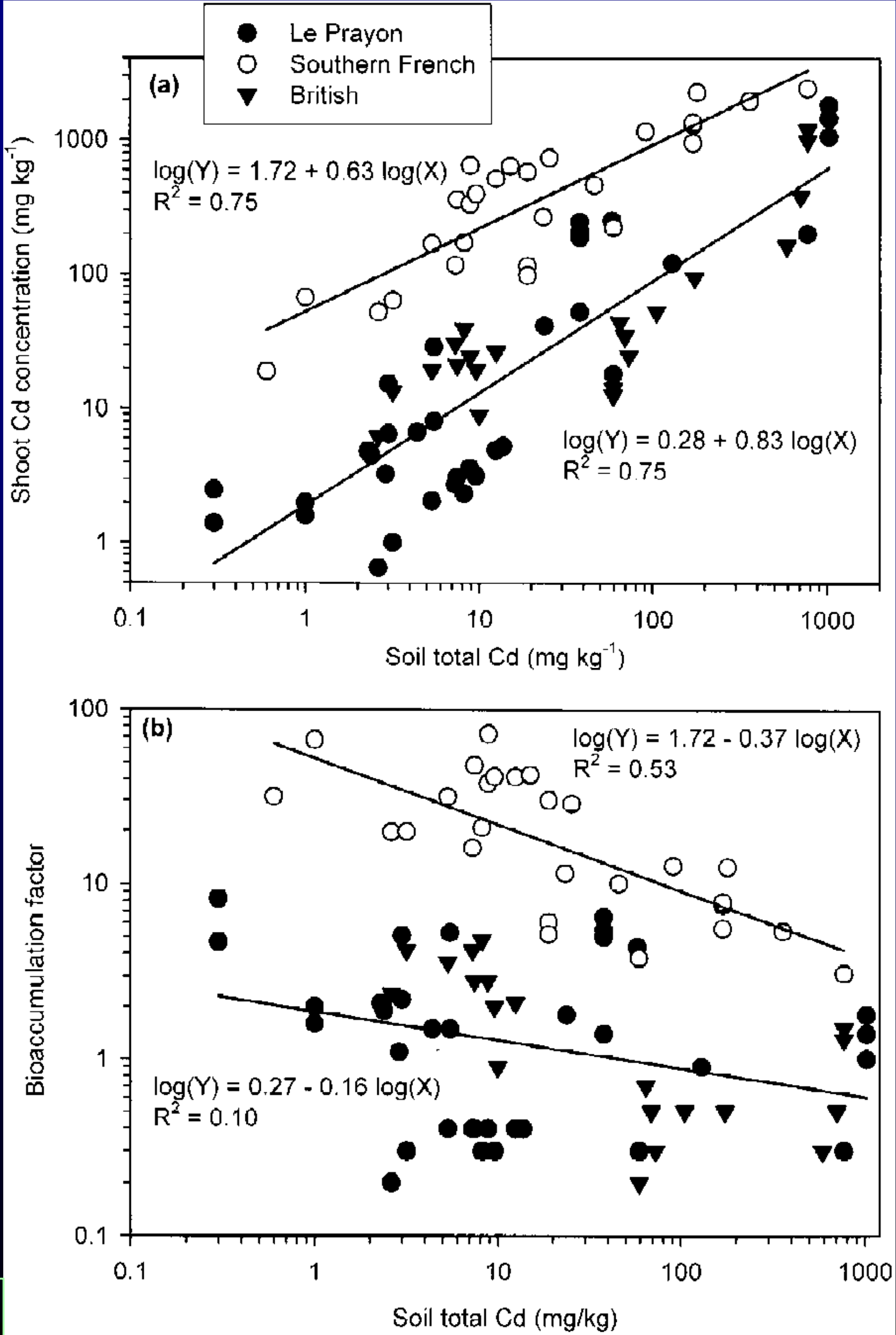
With 10 µM cadmium in the nutrient solution
--> healthy plants

Without cadmium in the nutrient solution
--> damage due to attack of insects

Küpper H, Kroneck PMH (2005) MIBS 44 (Sigel et al., eds), chapter 5

Accumulation of metals in CdZn-hyperaccumulators

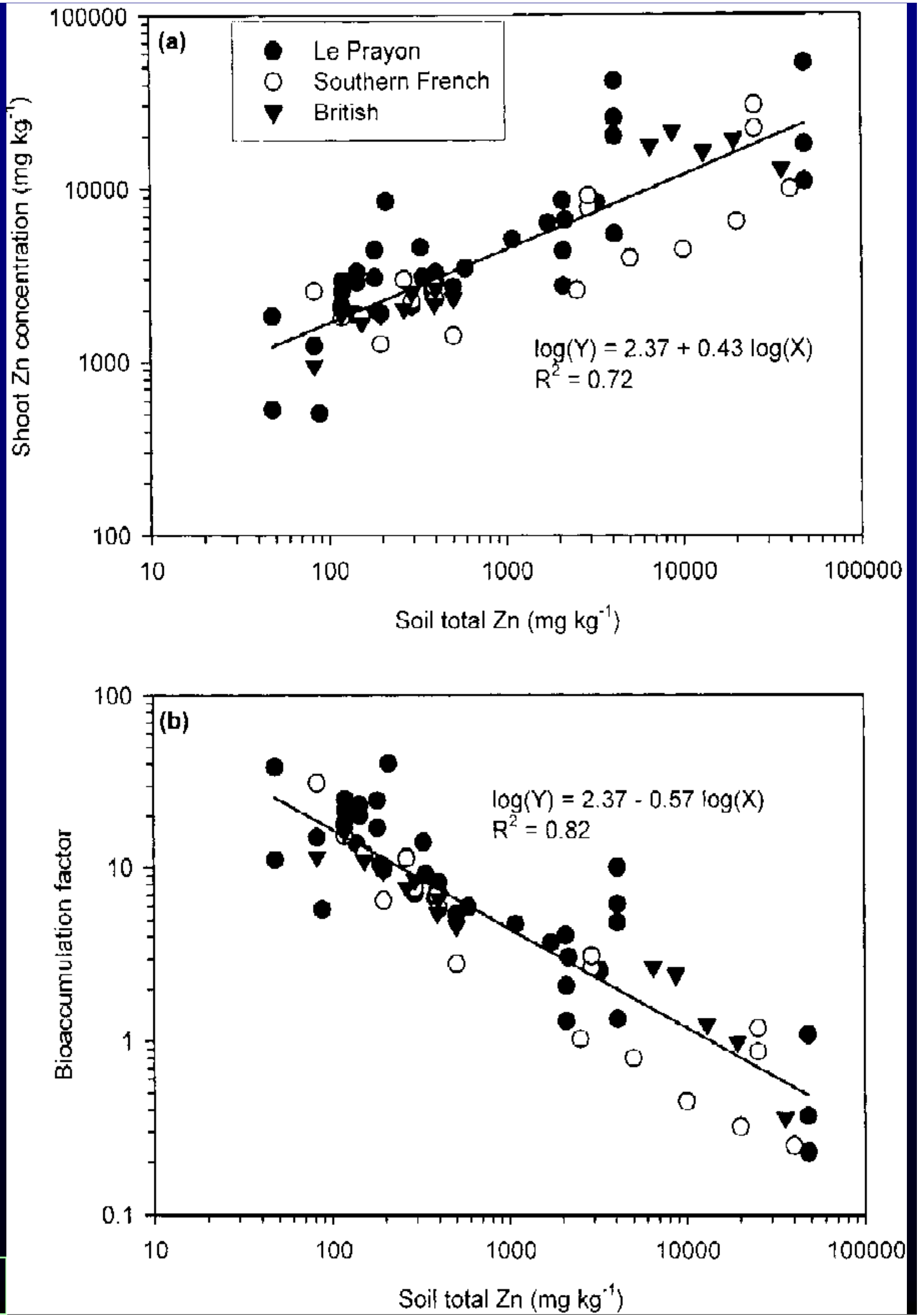
Bioaccumulation coefficients drastically vary between ecotypes of the same species, e.g. in *Thlaspi caerulescens* (Ganges ecotype vs. other ecotypes)
→ Potential for breeding!



Zhao FJ, Lombi E, McGrath SP(2003) Plant&Soil 249: 37-43

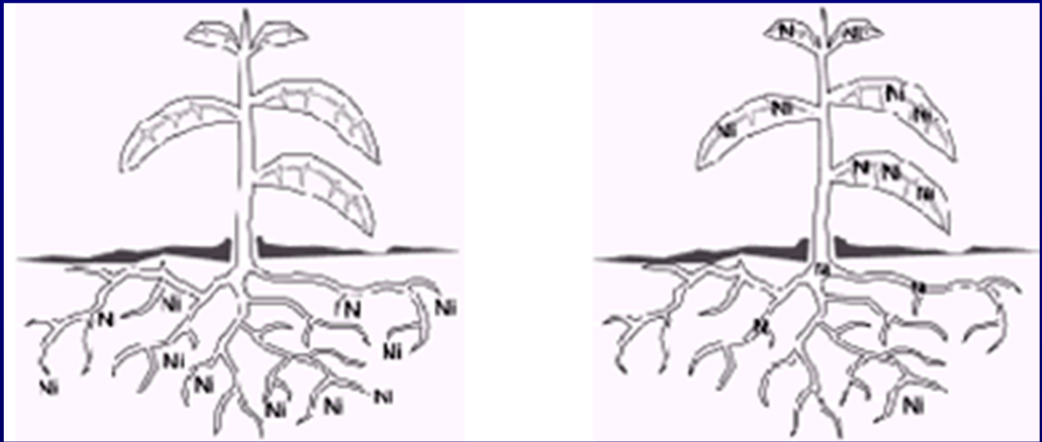
Accumulation of metals in CdZn-hyperaccumulators

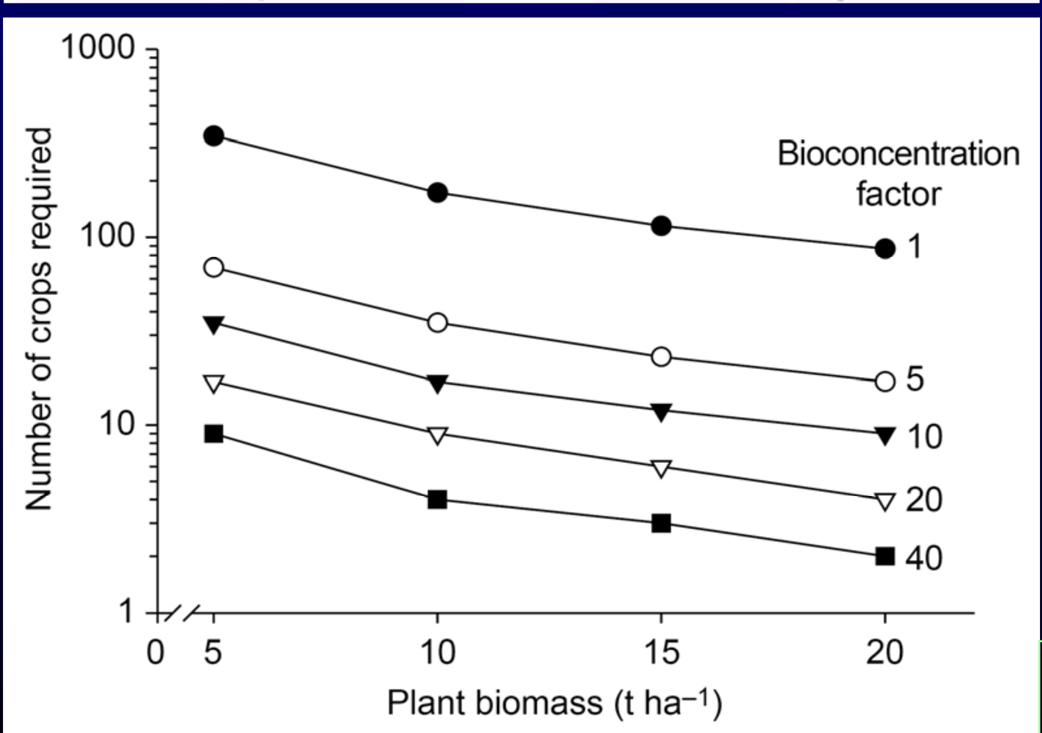
...but this does not apply to all metals!



Zhao FJ, Lombi E, McGrath SP(2003) Plant&Soil 249: 37-43

Use of Hyperaccumulators for cleaning up soils: Phytoremediation





→ Due to the high bioaccumulation coefficient of hyperaccumulators, metals are concentrated in a small amount of biomass.

McGrath SP, Zhao FJ (2003) Curr Opin Biotechnol 14: 277-82

Phytoremediation with different species

Plant species	Max. Cd mg/kg DW	Biomass t DW/ha	Cd-removal g/(ha*year)
Arabidopsis halleri	100	2	20
Thlaspi caerulescens (Prayon)	250	5	1250
***Thlaspi caerulescens* (S. France)**	**2500**	**5**	**12500**
Dichapetalum gelonoides	2.1	5	10
Athyrium yokosense	165	2	330
Arenaria patula	238	2	476
Sedum alfredii	180	5	900
Willow or poplar	**2.5**	**20**	**50**
Upland Rice	40.	10	400

Data from field experiments of Rufus Chaney (USA), presented on a conference in Hangzhou 2005

Chaney RL, et al (2005)
Z Naturforsch 60c, 190-8

Zn: Presume soil has 2000 ppm Zn = 4000 kg Zn (ha-15 cm)$^{-1}$

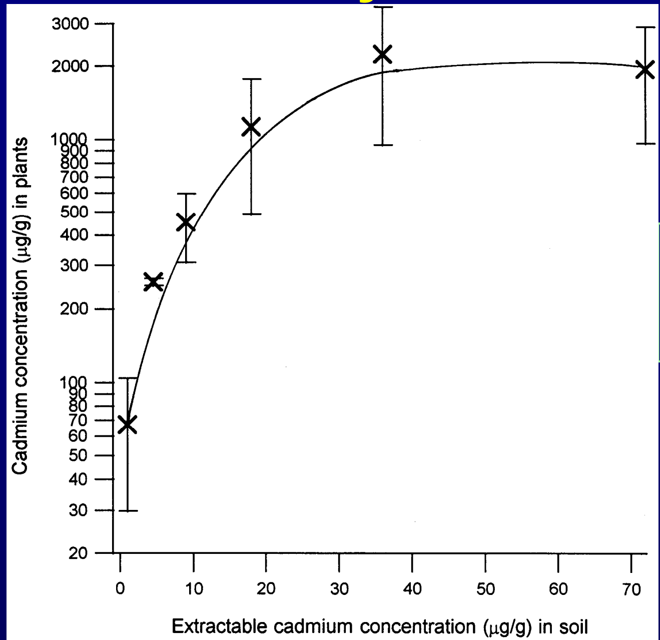
Crop	Yield [t ha^{-1}]	Zn in crop [mg kg^{-1}]	[kg ha^{-1}]	(% of soil Ni)	Zn in ash (%)
Corn (normal soil)	20	50	1.0	0.0025	0.10
Corn-Zn phytotoxicity	10	500	5.0	0.0125	0.50
Thlaspi	5	25000	125.	3.12	40
Improved *Thlaspi*	10	25000	250.	6.25	40

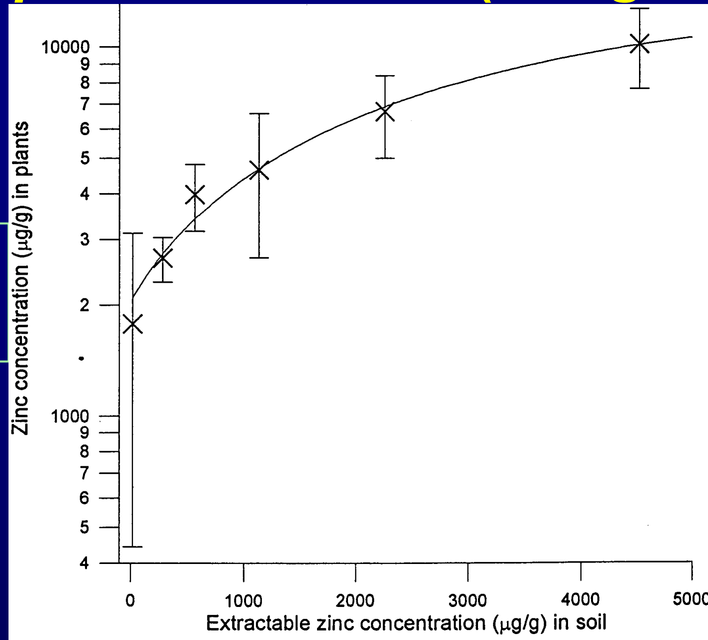
Cd: Presume soil has 20 ppm Cd = 40 kg Cd (ha-15 cm)$^{-1}$

Crop	Yield [t ha^{-1}]	Cd in crop [mg kg^{-1}]	[kg ha^{-1}]	(% of soil Cd)	Cd in ash (%)
Corn	20	0.5	0.01	0.025	0.001
Corn	10	5	0.05	0.125	0.005
Thlaspi ‘Prayon’	5	200	1.0	2.5	0.40
Thlaspi S. France	5	2000	10.0	25.	4.00
Thlaspi Improved	10	2000	20.0	50.	4.00

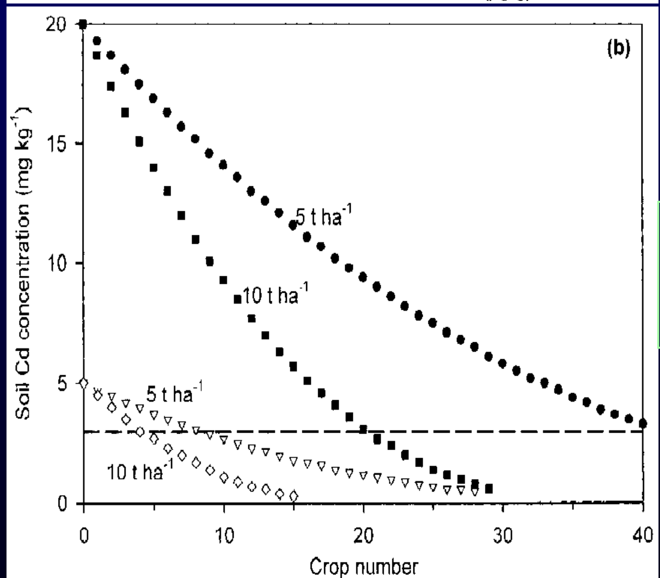
→ Due to its high bioaccumulation coefficient and despite its small biomass, *Thlaspi caerulescens* (Ganges ecotype) is so far the best plant for Cd phytoremediation

Cd and Zn Phytoremediation with *Thlaspi caerulescens* (Ganges)

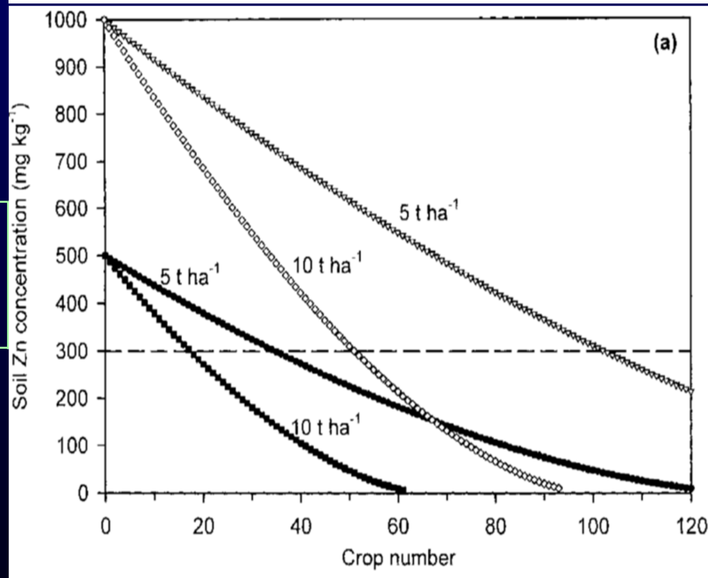




Robinson BH_et al et Brooks RR (1998) Plant & Soil 203, 47-56

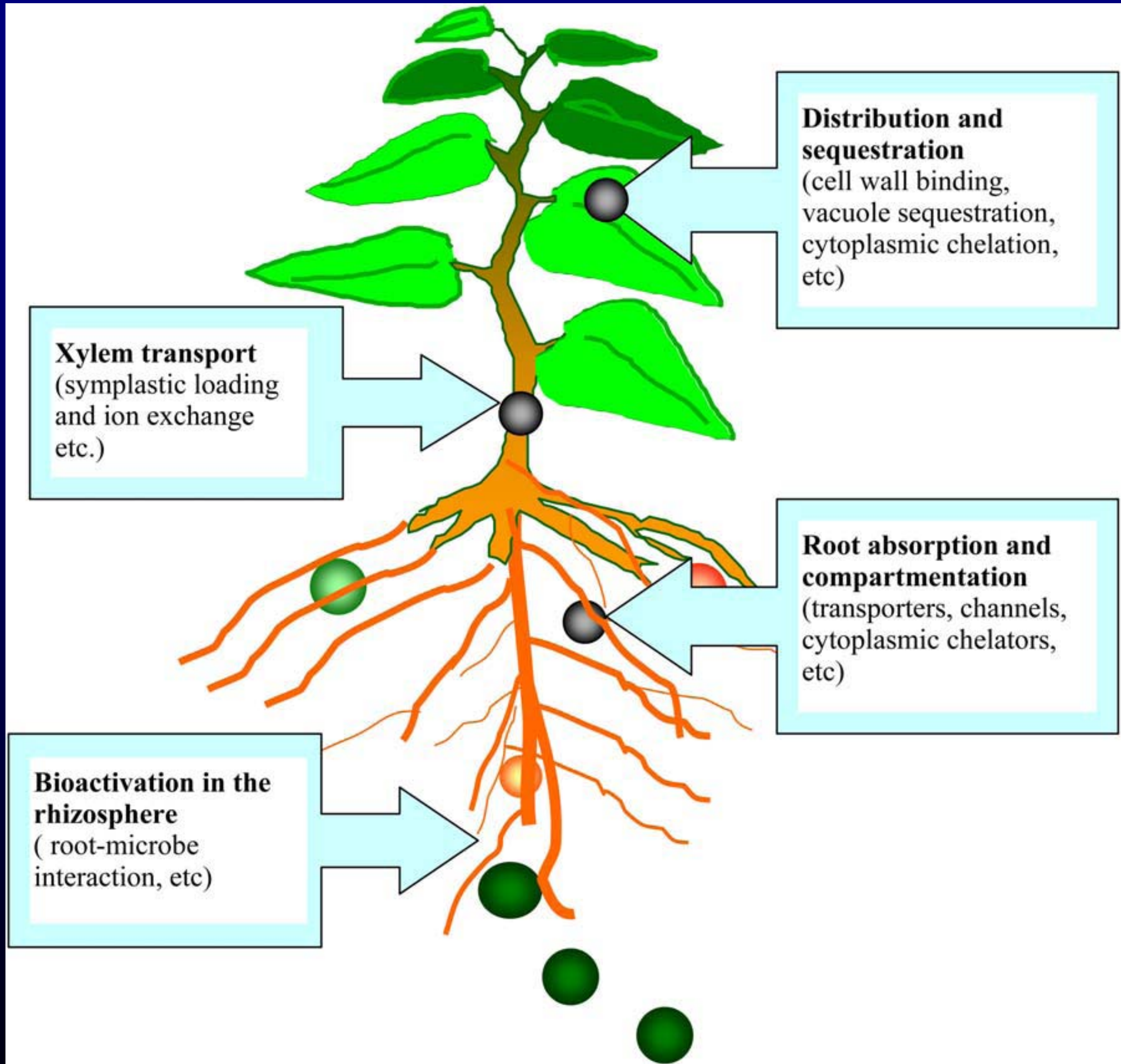


Zhao FJ, Lombi E, McGrath SP(2003) Plant&Soil 249: 37-43



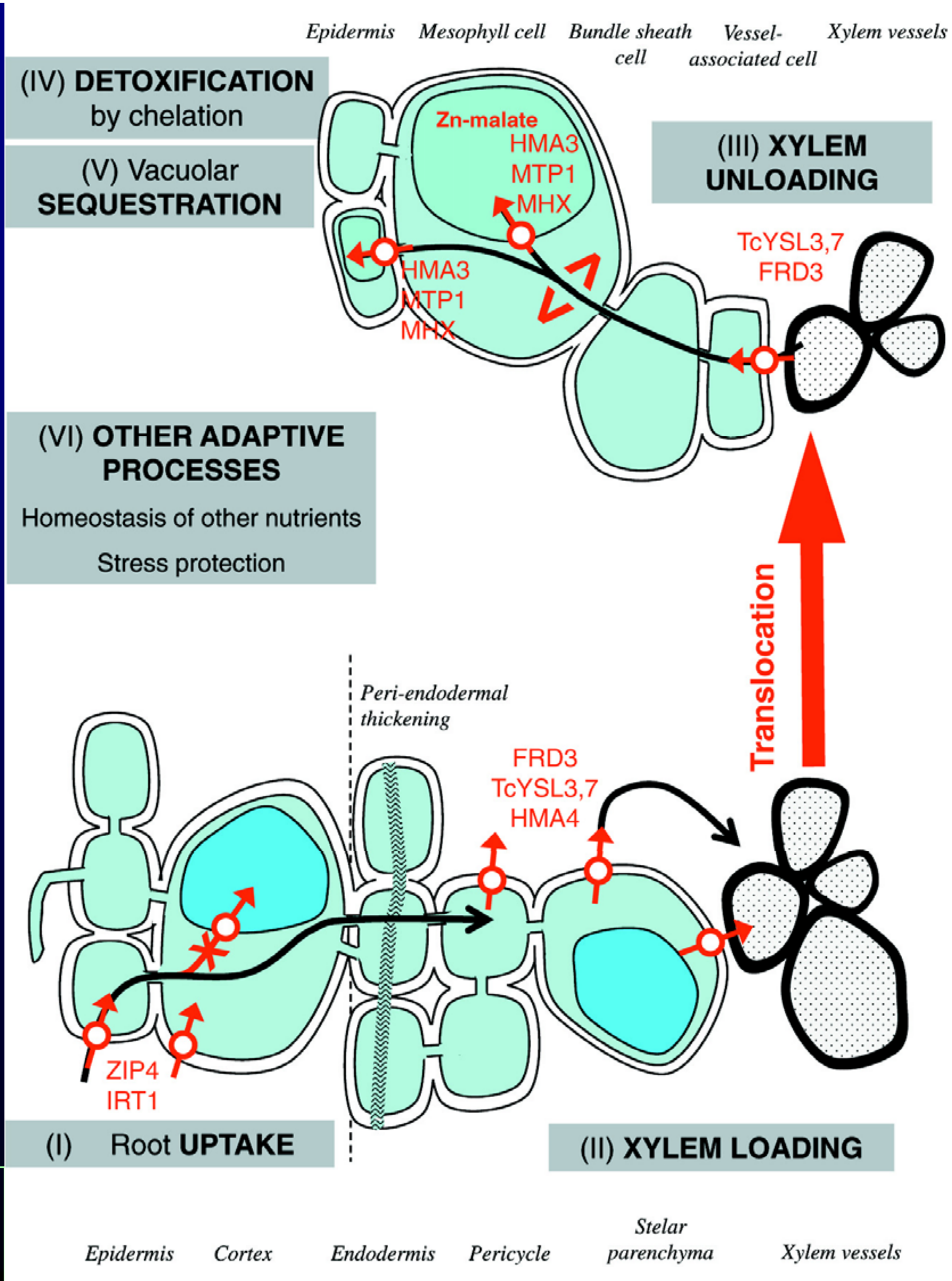
→ While Cd phytoremediation is efficient with *Thlaspi caerulescens,* Zn phytoremediation is inefficient due to lower bioaccumulation coefficient and high soil Zn

Use of Hyperaccumulators for cleaning up soils: Factors influencing phytoremediation capacity of plants



Yang X, Feng Y, He Z, Stoffella PJ (2005) J Trace Elem Med Biol 18, 339-53

Use of Hyperaccumulators for cleaning up soils: passage of metals in plants & genes involved in some steps



Verbruggen N, Hermans S, Schat H (2009) New Phytol 181, 759-96

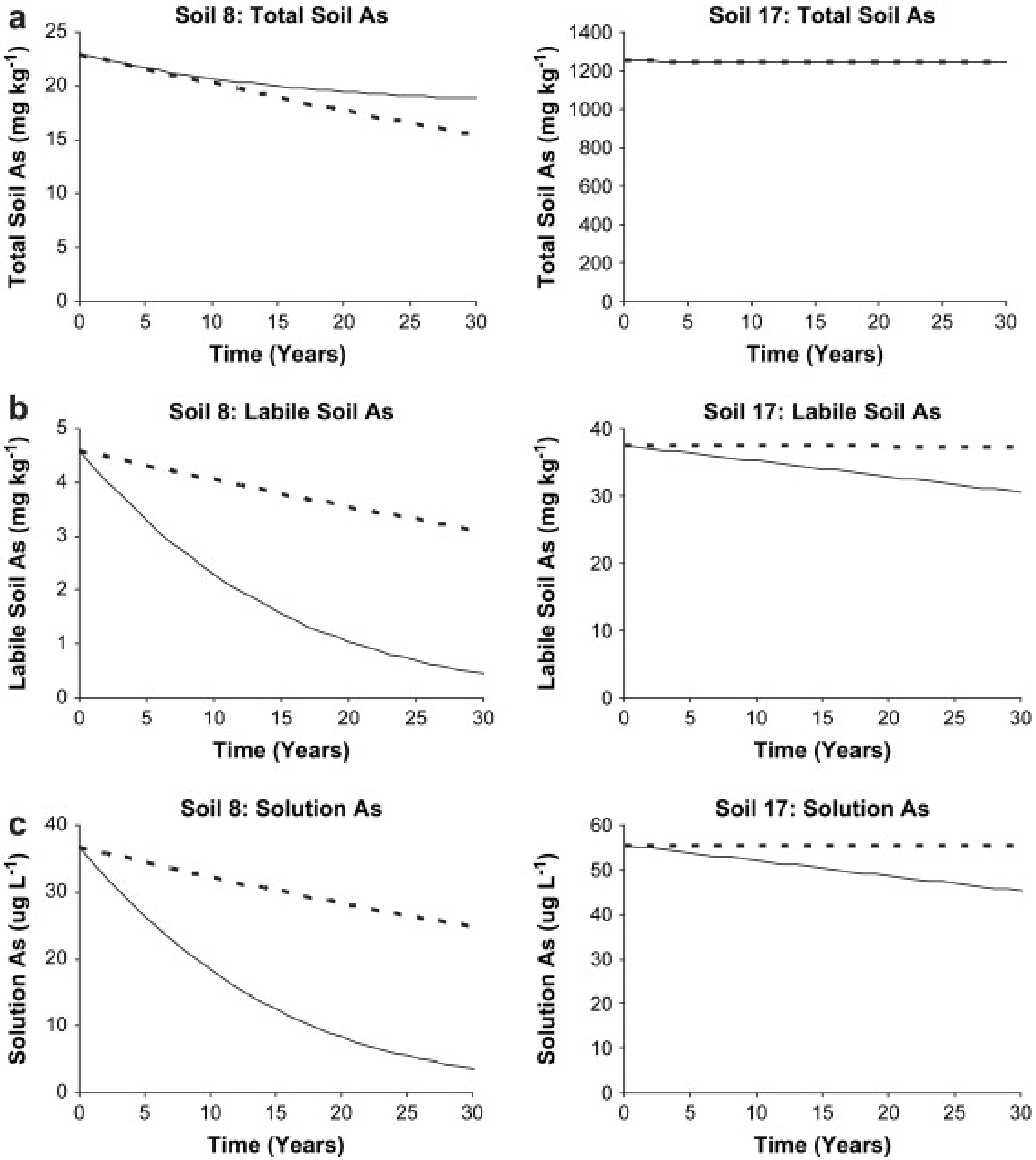
Soil factors influencing phytoremediation – pH and labile metal

→ if labile pool is constantly replenished, labile contaminant in soil decreases slower, but total soil contamination decreases faster than in the case of a fixed labile pool

→ detoxification of As works much better
in alkaline soils (soil 8: pH 8.1)
than
in acidic soils (soil 17: pH 5.6)

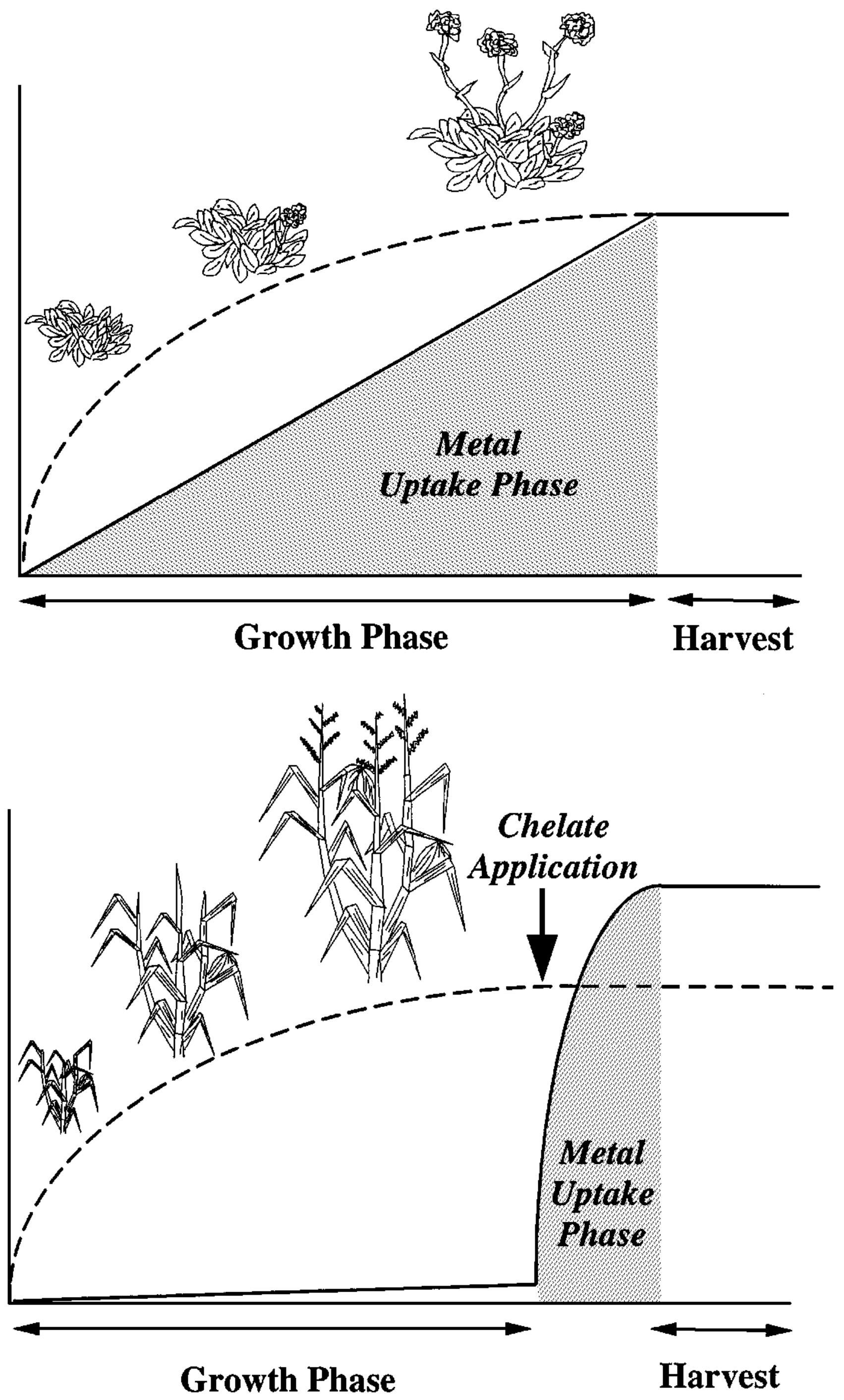
Shelmerdine P, et al. (2009) Environ Pollut 157, 1589-1596

dashed lines: constant equilibrium
solid lines: no replenishment of labile pool



Variants of phytoremediation: continuous vs. chelate-assisted

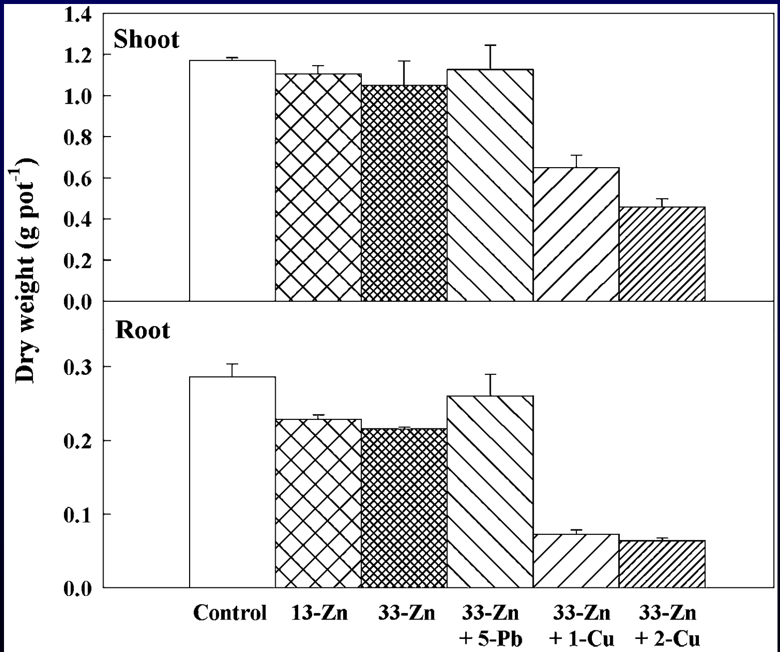
→if labile pool is very small, phytoremediation may be enhanced by chelate application

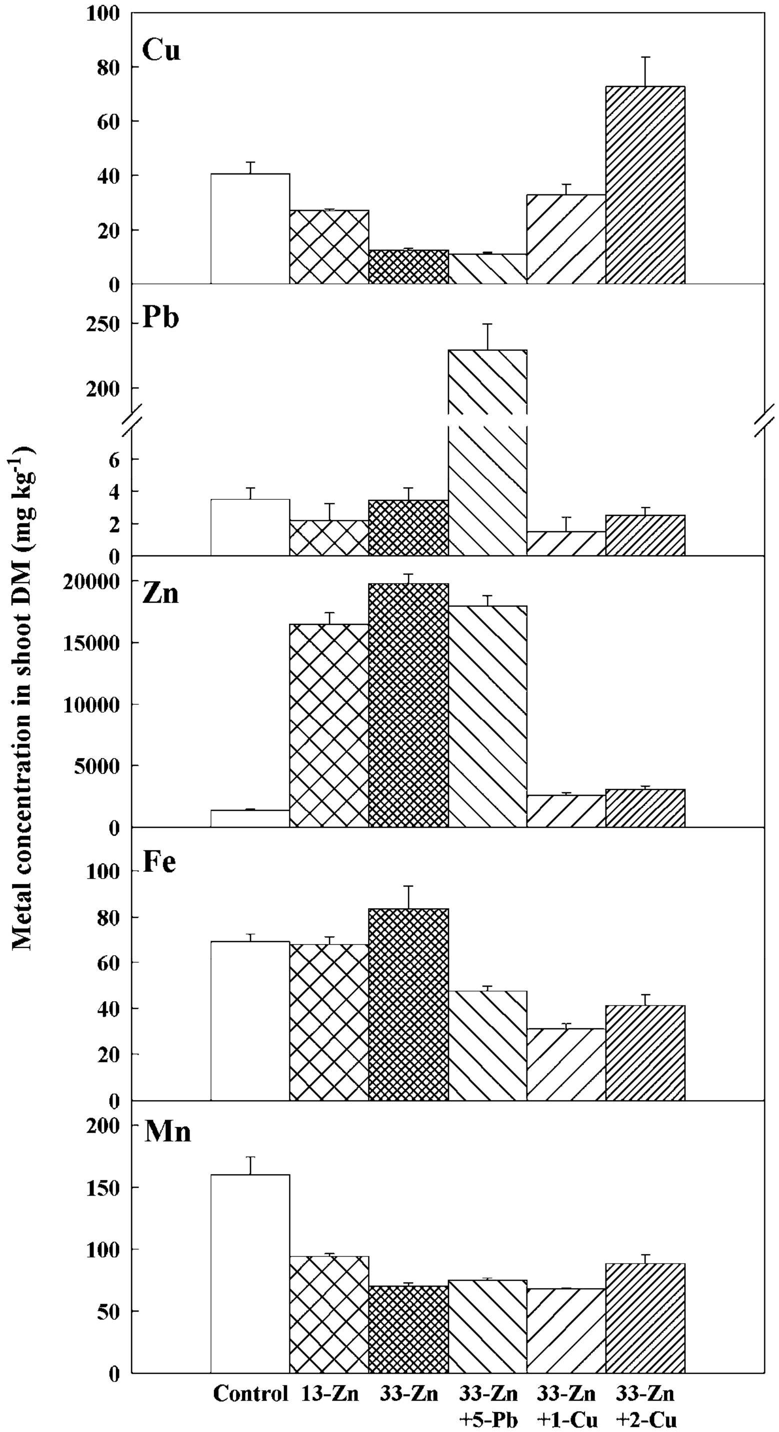


Salt DE, Smith RD, Raskin I (1998) Ann Rev Pl Phys Pl Mol Biol 49, 643-68

Soil factors influencing phytoremediation – toxic metals

→ toxic non-accumulated metals (e.g. Cu for *T. caerulescens*) inhibit plant growth and diminish uptake of hyperaccumulated metals





Walker DJ, Bernal MP (2004) Water Air Soil Pollut 151, 361-72

Soil factors influencing phytoremediation – toxic metals

→ selection of resistant individuals may solve the problems of co-contamination of soils with non-accumulated toxic metals

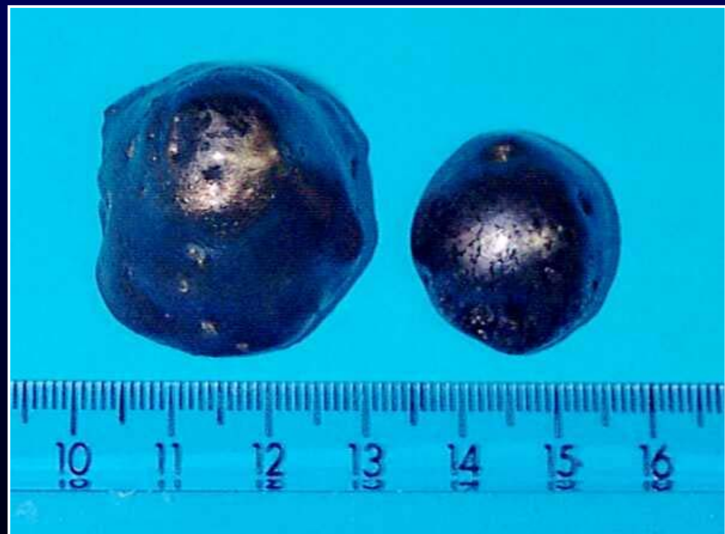
Mijovilovich A, Leitenmaier B, Meyer-Klaucke W, Kroneck PMH, Götz B, Küpper H (2009) Plant Physiology 151, 715-731

Phytoextraction in action

The location: a base-metal smelter, South Africa

The problem: Ni contamination over 5ha due to Ni salt storage and spillage

The solution: phytoextraction using a native nickel-accumulating species



From: Presentation of Chris Anderson at CERM3 meeting

Application of hyperaccumulators for phytomining

Vegetation on naturally nickel-rich soil (Serpentine). Such soil is neither usable for agriculture (Ni-concentration far too high) nor for conventional ore mining (Ni-concentration too low).

Nickel-hyperaccumulators on such soils enrich the Ni to several percent of their shoot dry mass. After burning them, the ash contains 10 to 50% Ni, so that it can be used as a „bio-ore“.

Phytomining pictures from R. Chaney

Such a plant mine can, according to field studies under commercial conditions, yield around 170 kg Ni per hectare and year. At the current (average Jan-July 2012) Ni price of around 14 € per kg raw nickel these are about 2400 € per hectare and year.

Phytomining with different species

Table I. Crop and hyperaccumulator plant models for Ni phytomining. The second *Alyssum murale* listing presumes that plant breeding has been used to develop a commercial cultivar for phytomining Ni (Li *et al.*, 2003). Maize is modeled as a forage crop; ash weight is about 5–10% of dry weight.

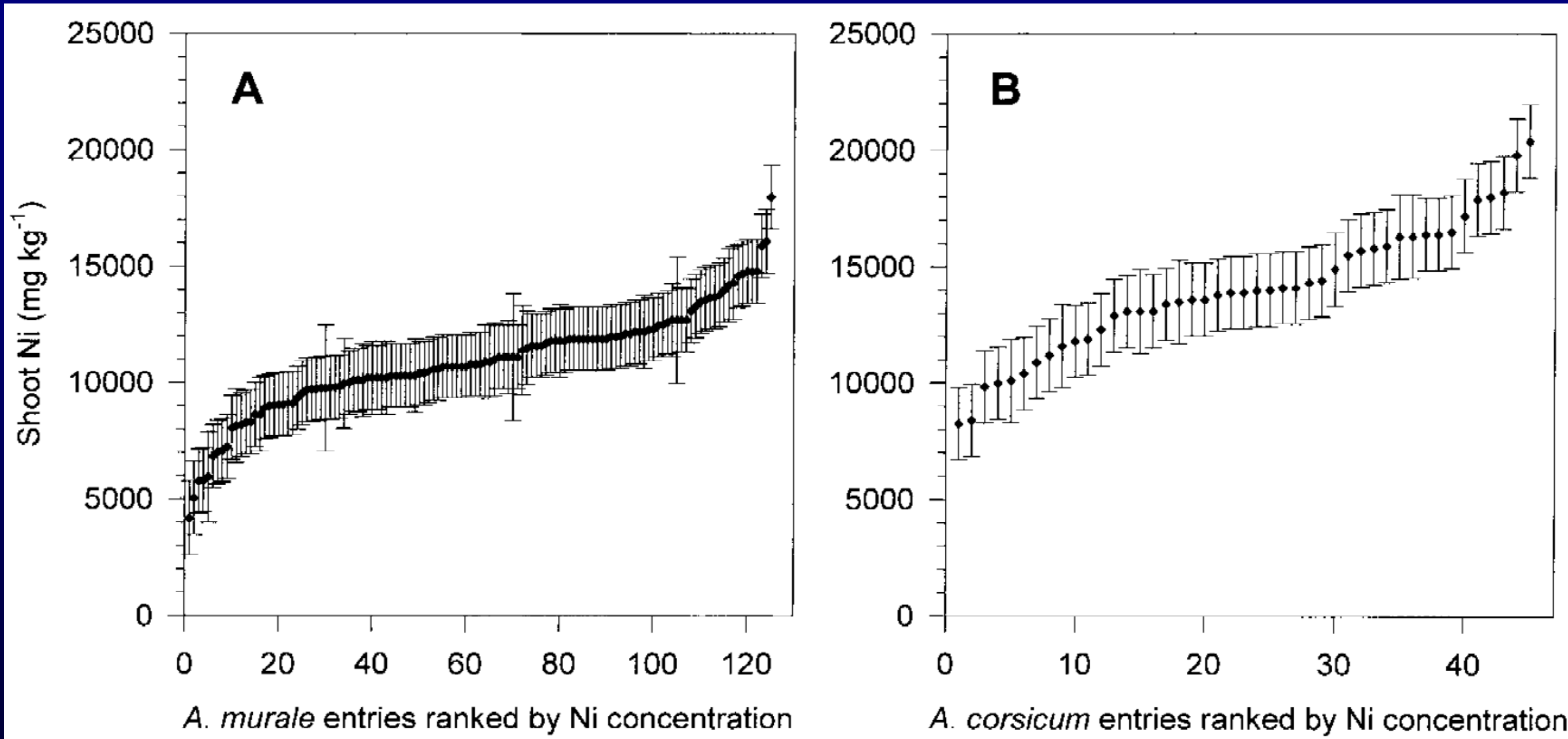
Assume soil contains 2500 mg Ni kg^{-1} = 10,000 kg Ni $(ha\text{-}30\ cm)^{-1}$

Species	Yield	Ni in the crop			Ash–Ni
	[t ha^{-1}]	[mg kg^{-1}]	[kg ha^{-1}]	(% of soil Ni)	(%)
Maize (100% normal)	20	2	0.04	0.0004	0.008
Maize (50% normal yield)	10	100	1	0.01	0.20
Wild *Alyssum*	10	20,000	200	2.0	20–40
Alyssum cultivar	20	30,000	600	6.0	25–50

Chaney RL, et al et Baker AJM (2005) ZNaturforsch60c, 190-198

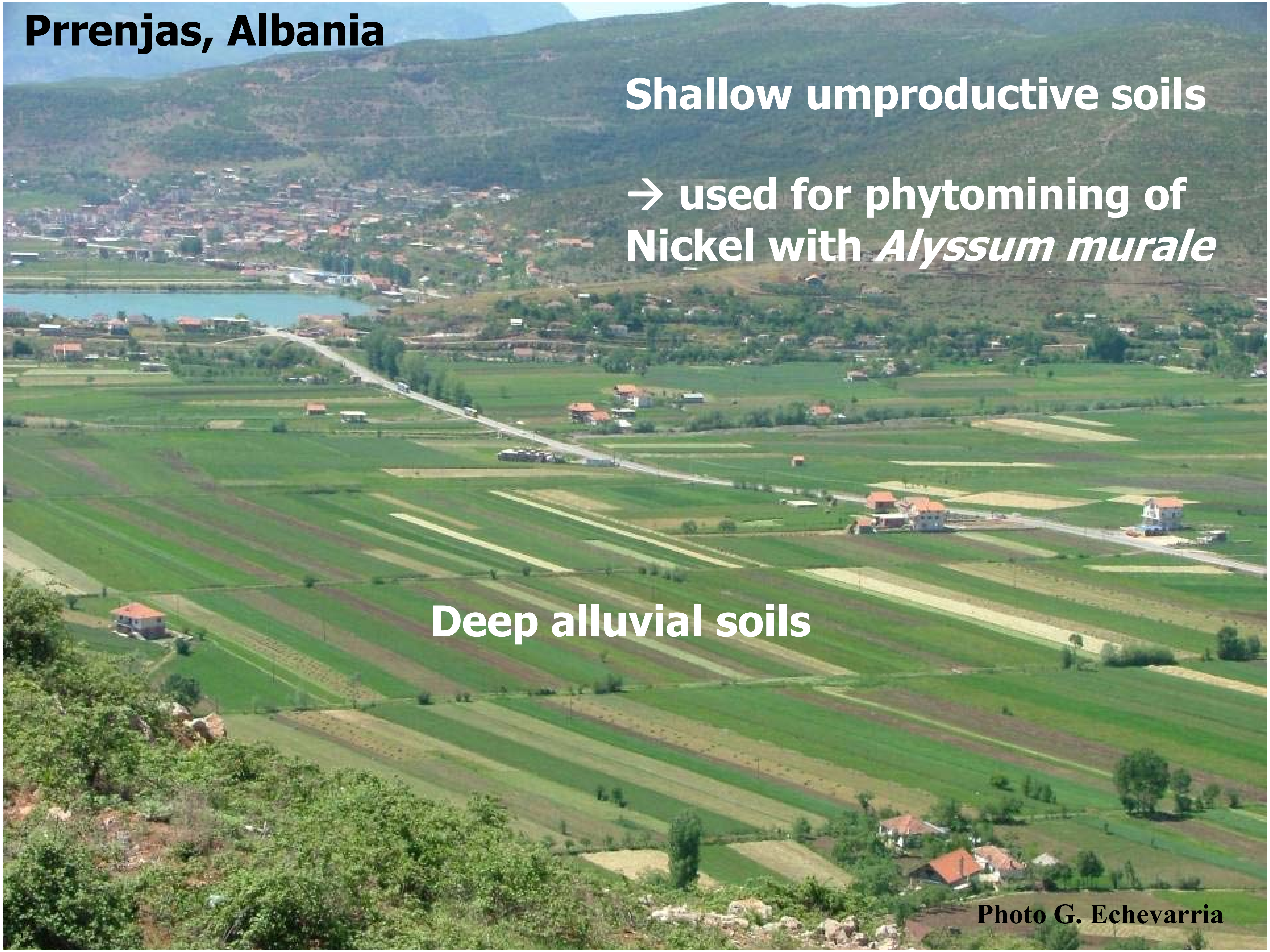
→ Due to their high bioaccumulation coefficient and despite their small biomass, already wild *Alyssum* species yield many times more nickel per heactare than high-biomass non-accumulator plants, and in contrast to the latter the ash of *Alyssum* contains enough Ni to be used as an ore

Phytomining: potential of selecting plant populations with highest phytoextraction



Li YM, Chaney R, et al et Baker A et Reeves R (2003) Plant & Soil 249, 107-15

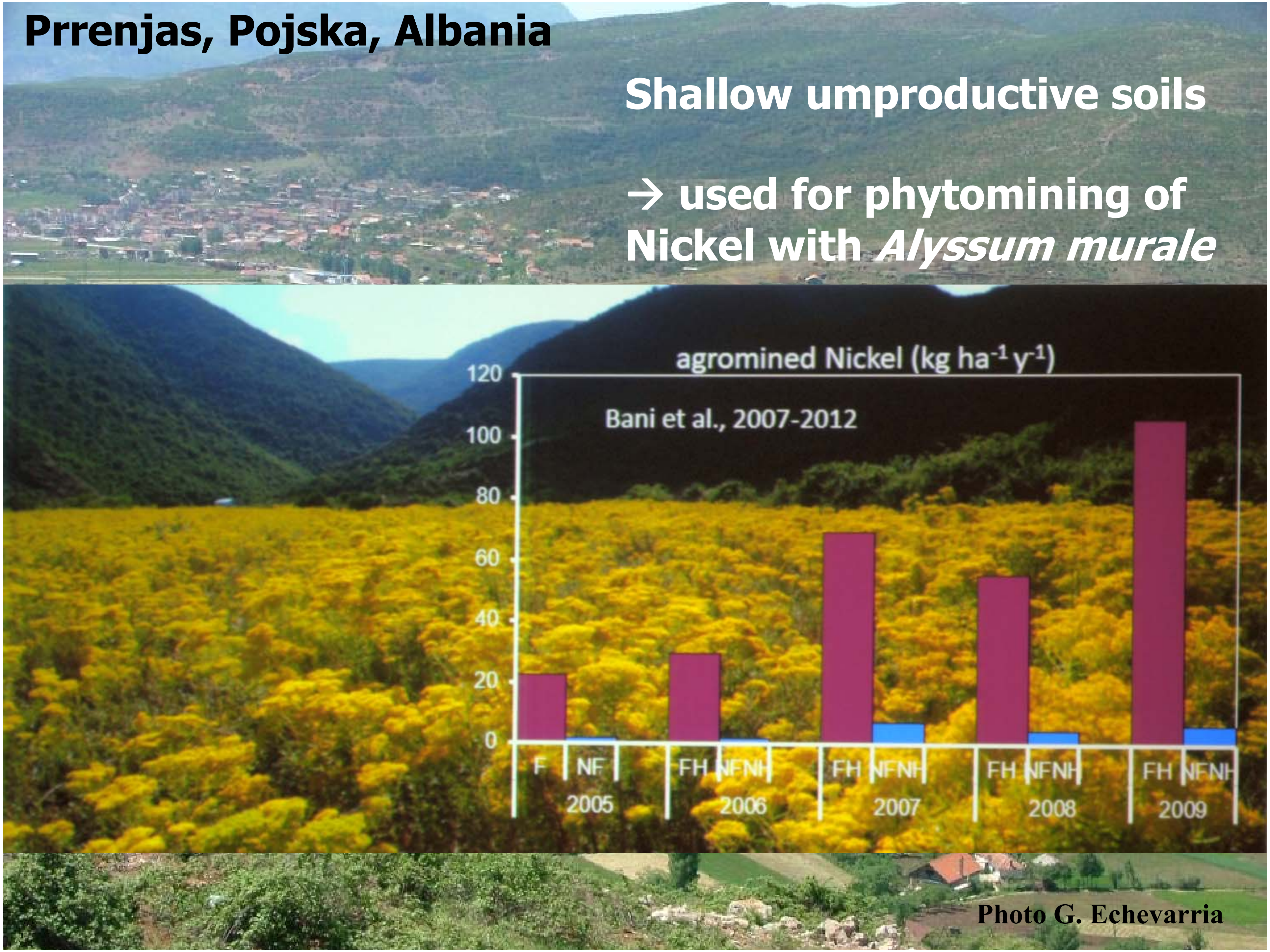
→ large variation in metal accumulation between populations of hyperaccumulator species allows for efficient selection of high-yield ecotypes


Prrenjas, Albania
Shallow umproductive soils
→ used for phytomining of Nickel with *Alyssum murale*
Deep alluvial soils
Photo G. Echevarria

Prrenjas, Albania

Shallow umproductive soils

→ used for phytomining of Nickel with *Alyssum murale*


Prrenjas, Pojska, Albania
Shallow umproductive soils
→ used for phytomining of Nickel with *Alyssum murale*
agromined Nickel (kg ha-1 y-1)
Bani et al., 2007-2012
120
100
80
60
40
20
0
F NF
2005
FH NFNH
2006
FH NFNH
2007
FH NFNH
2008
FH NFNH
2009
Photo G. Echevarria

Economic evaluation of Ni phytomining based on 69kg Ni per ha

- With adapted agricultural practices :
  - Biomass production : 6 t per ha
  - Ni concentration : 1,15%
- Phytoextraction : 69 kg Ni per ha
- If:
  - Production costs: $\$390\ ha^{-1}$
  - Land loan: $\$150\ ha^{-1}$
  - Commercial value of Ni $\$24\ kg^{-1}$ (2008)
  - Recovery (e.g. hydrometallurgy) : 20% of Ni value
- Then : annual value of a phytomining crop :
  - 69 kg Ni ha^{-1} x $\$24\ kg^{-1}$ Ni = **$\$ 1\ 656\ ha^{-1}$**
- Economic result :
  - 1656 – (390 + 150) = **$\$ 1\ 116\ ha^{-1}$**

Therefore: phytomining of Ni offers a financial revenue to farmers on areas with low agricultural potential

Bani, Aida & Barbaroux, Romain & Simonnot, Marie-Odile & Mercier, Guy & Blais, Jean-François & Plasari, Edouard & Echevarria, Guillaume & Morel, Jean-Louis. (2011). Phytomining, a means for soil remediation and metal recovery. The case of nickel.

Phytomining in the tropics

First agromining field trial at Pahu (Sabah - Malaysia) – 1.5 ha with *Rinorea bengalensis* + *Phyllanthus rufuschaneyi*.

Characteristics	*Rinorea bengalensis*	*Phyllanthus rufuschaneyi*
Size	30 m tree	3 m shrub
Maximum Ni concentration in leaves	2.7%	6%
Propagation	Seeds	Cuttings

→ Use of woody species for phytomining soils in Malaysia, yield: approx 270 kg Ni/ha

Talk of Alan Baker at ICOBTE in Nanjing, 2019

Phytomining in the tropics

The first tropical 'metal farm': *Phyllanthus rufuschaneyi*

After 1.5 years → No harvesting

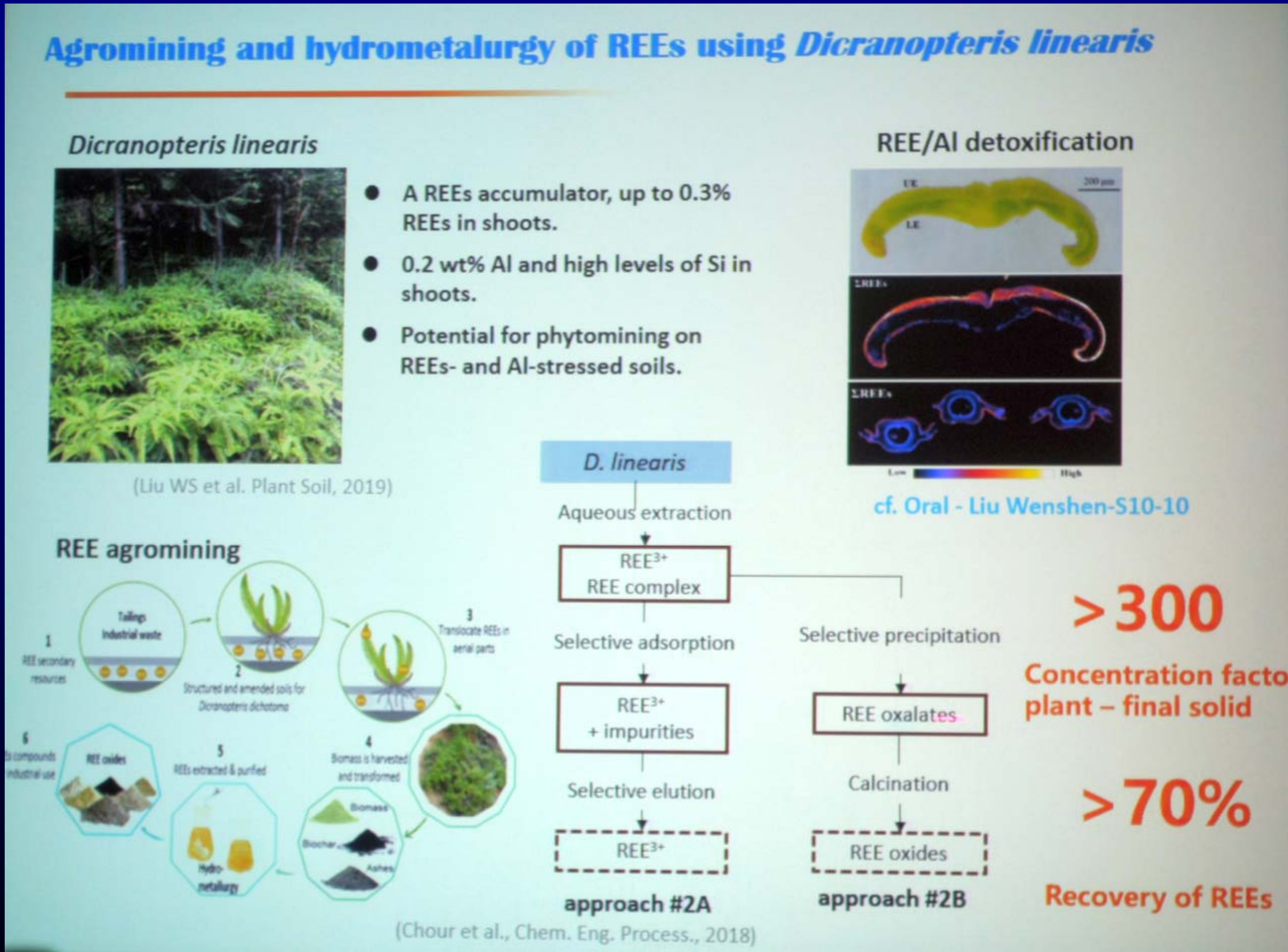
(Van der Ent, 2016-2018)

→ Use of woody species for phytomining soils in Malaysia, yield: approx 270 kg Ni/ha

Characteristics	*Rinorea bengalensis*	*Phyllanthus rufuschaneyi*
Size	30 m tree	3 m shrub
Maximum Ni concentration in leaves	2.7%	6%
Propagation	Seeds	Cuttings

Talk of Alan Baker at ICOBTE in Nanjing, 2019

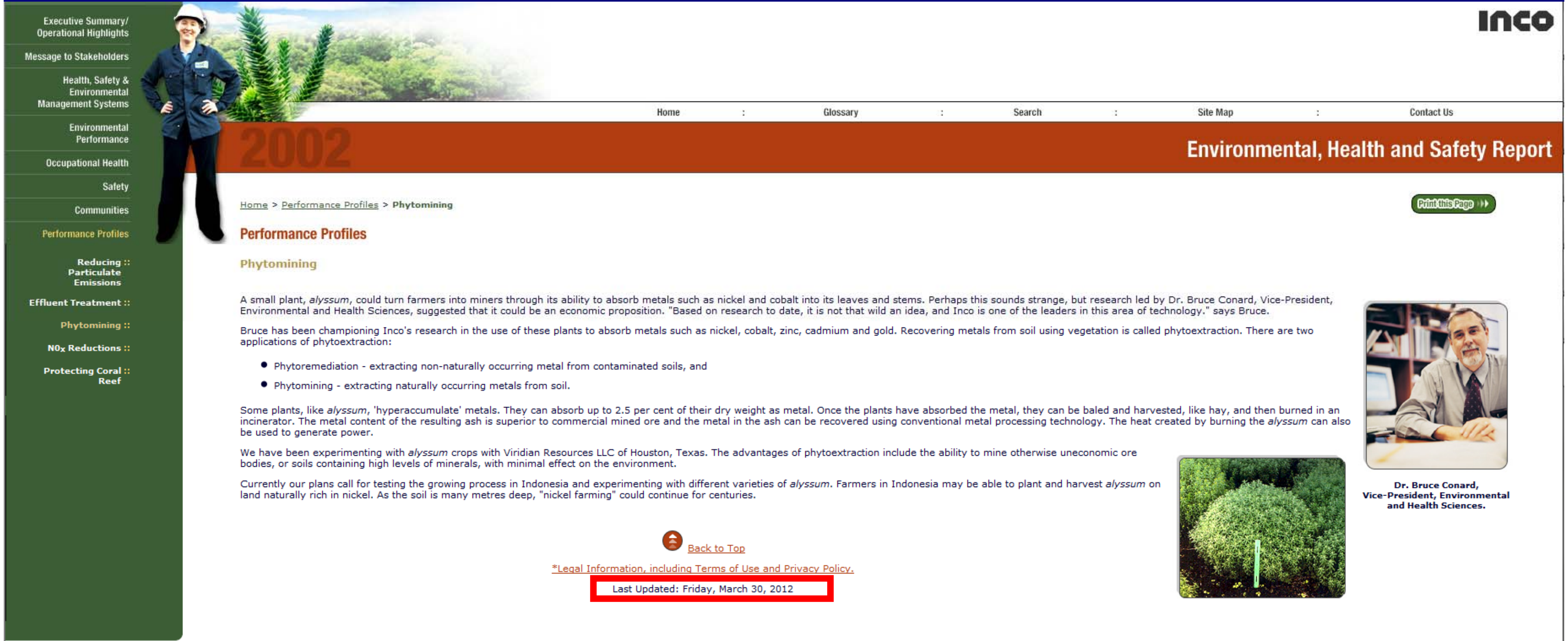
Phytomining in China



Talk of Chour at ICOBTE in Nanjing, 2019

One big mining company currently employing phytomining

http://nickel.vale.com/development/reports/ehs/2002/performance_profiles/phytomining/Default.asp



INCO

Executive Summary/ Operational Highlights
Message to Stakeholders
Health, Safety & Environmental Management Systems
Environmental Performance
Occupational Health
Safety
Communities
Performance Profiles
Reducing :: Particulate Emissions
Effluent Treatment ::
Phytomining ::
NOx Reductions ::
Protecting Coral :: Reef

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2002 Environmental, Health and Safety Report

Home > Performance Profiles > Phytomining

Print this Page

Performance Profiles

Phytomining

A small plant, *alyssum*, could turn farmers into miners through its ability to absorb metals such as nickel and cobalt into its leaves and stems. Perhaps this sounds strange, but research led by Dr. Bruce Conard, Vice-President, Environmental and Health Sciences, suggested that it could be an economic proposition. "Based on research to date, it is not that wild an idea, and Inco is one of the leaders in this area of technology." says Bruce.

Bruce has been championing Inco's research in the use of these plants to absorb metals such as nickel, cobalt, zinc, cadmium and gold. Recovering metals from soil using vegetation is called phytoextraction. There are two applications of phytoextraction:

- Phytoremediation - extracting non-naturally occurring metal from contaminated soils, and
- Phytomining - extracting naturally occurring metals from soil.

Some plants, like *alyssum*, 'hyperaccumulate' metals. They can absorb up to 2.5 per cent of their dry weight as metal. Once the plants have absorbed the metal, they can be baled and harvested, like hay, and then burned in an incinerator. The metal content of the resulting ash is superior to commercial mined ore and the metal in the ash can be recovered using conventional metal processing technology. The heat created by burning the *alyssum* can also be used to generate power.

We have been experimenting with *alyssum* crops with Viridian Resources LLC of Houston, Texas. The advantages of phytoextraction include the ability to mine otherwise uneconomic ore bodies, or soils containing high levels of minerals, with minimal effect on the environment.

Currently our plans call for testing the growing process in Indonesia and experimenting with different varieties of *alyssum*. Farmers in Indonesia may be able to plant and harvest *alyssum* on land naturally rich in nickel. As the soil is many metres deep, "nickel farming" could continue for centuries.

Dr. Bruce Conard, Vice-President, Environmental and Health Sciences.

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Last Updated: Friday, March 30, 2012

→ Use of *Alyssum* species for phytomining soils in Indonesia

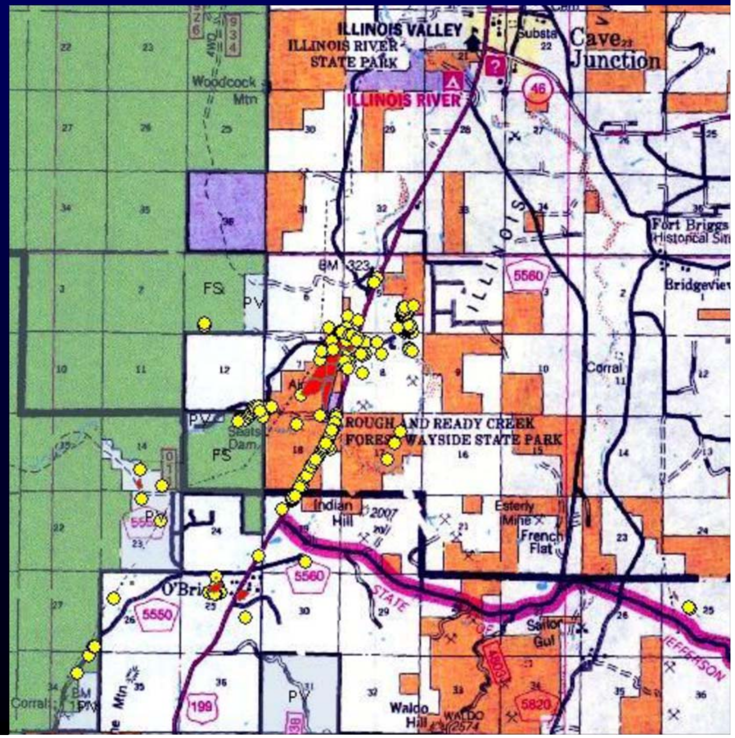
...And another one that tested phytomining, but did a bad job → Hyperaccumulators as invasive species!

http://www.co.josephine.or.us/Files/AlyssumStory.pdf

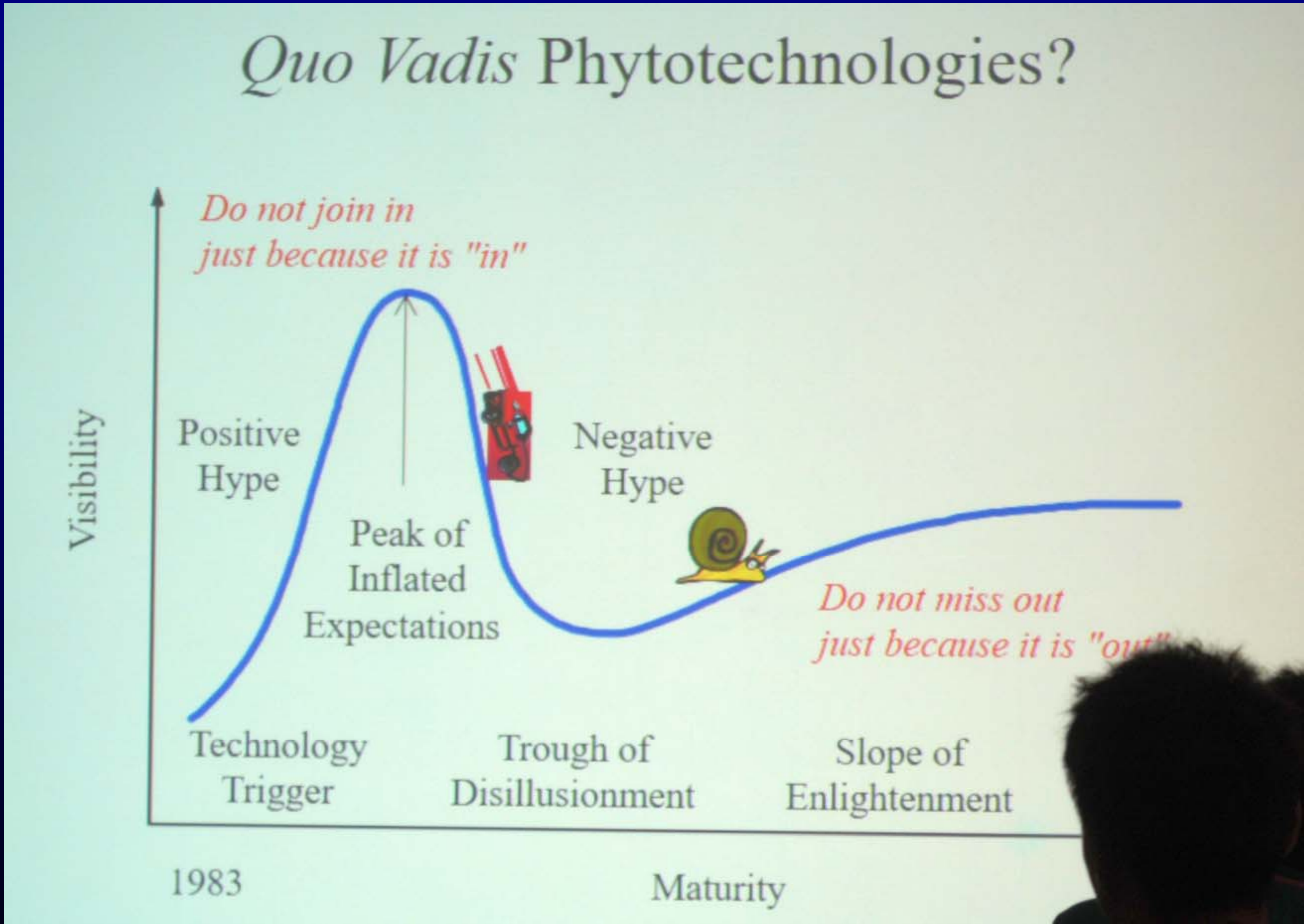
- In the late 1990's Alyssum was introduced to the Illinois Valley at an experimental site by USDA, OSU and Viridian LLC
- 2002 Viridian Resources LLC planted 9 sites near O'Brien, OR
- 2005 Alyssum found growing wild and far from planted sites
- 2009 Alyssum murale and A. corsicum petitioned for listing, then listed, as a noxious weed in OR
- 2009 -2010 Large scale control efforts begin, including planted sites abandoned by Viridian Resources

red: planted sites (2002)

yellow: escaped sites (2010)



Summary



Talk of A Baker at ICOBTE in Nanjing, 2019; van der Ent A (2021) Agromining - farming for metals_Springer ISBN978-3-030-58904-2

All slides of my lectures can be downloaded from my workgroup homepage

Biology Centre CAS → Institute of Plant Molecular Biology → Departments → Department of Plant Biophysics and Biochemistry,

or directly

http://webserver.umbr.cas.cz/~kupper/AG_Kuepper_Homepage.html