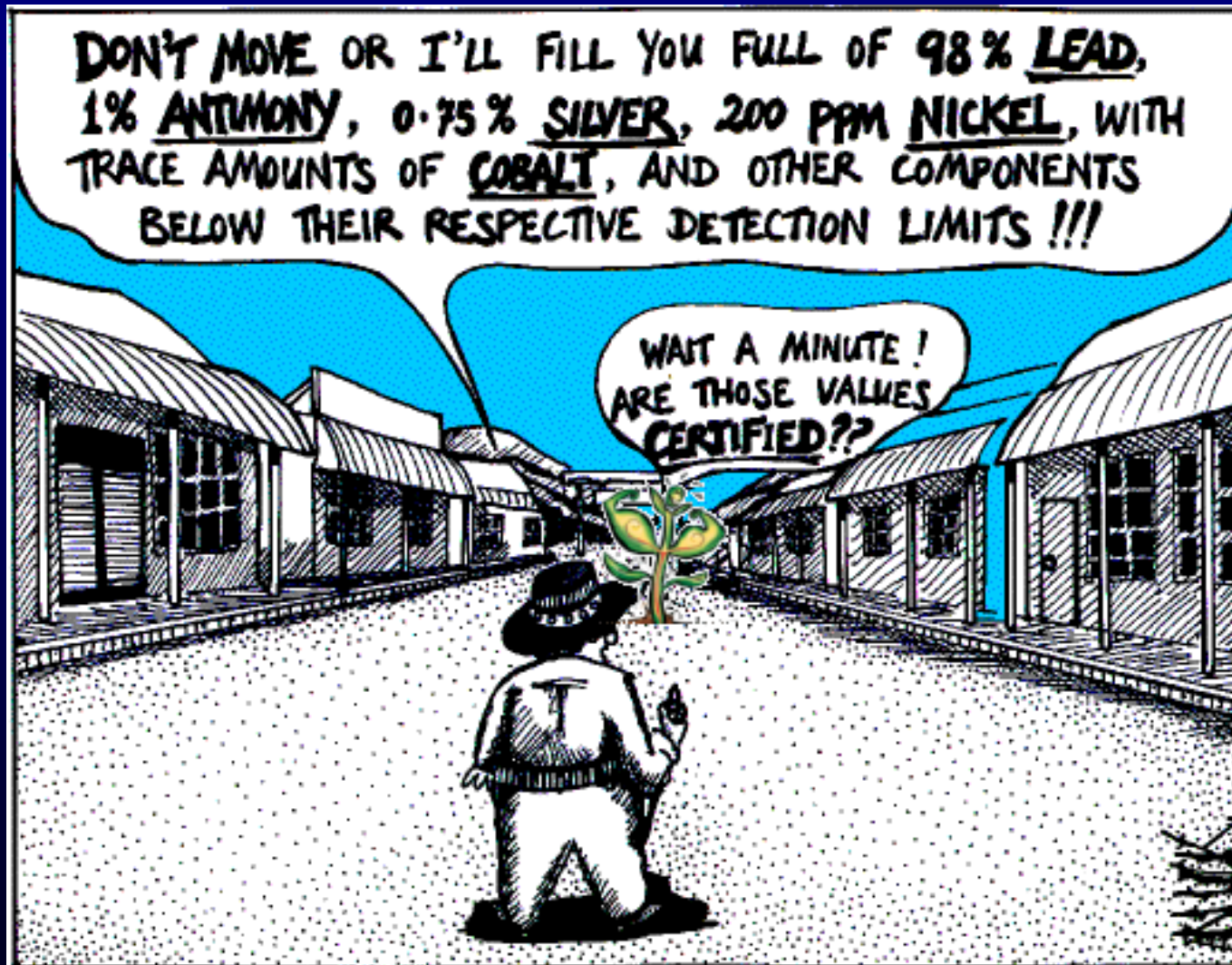


Heavy Metals and Plants - a complicated relationship

→ Biotechnological use of heavy metal accumulation in plants



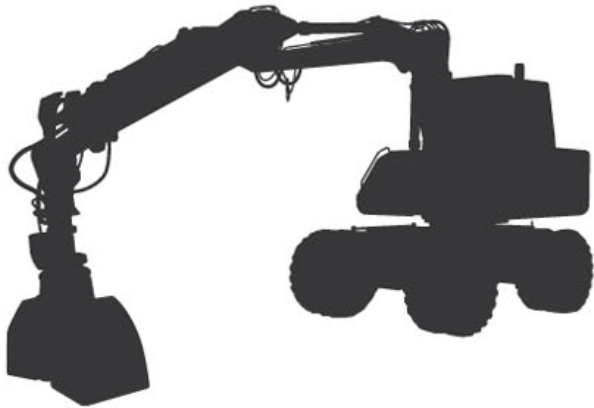
Heavy metal-hyperaccumulation in the Wild West

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)

Excavation and Fill

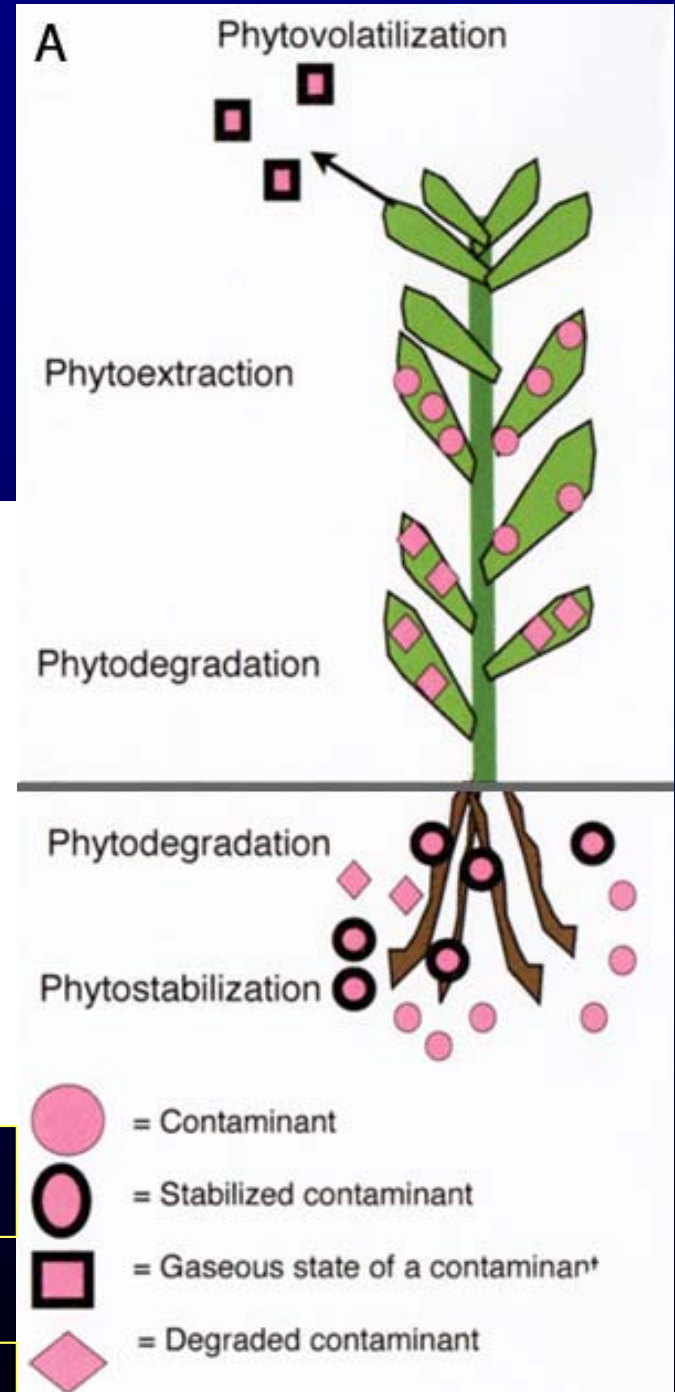


\$50,000 - 100,000

Phytoextraction



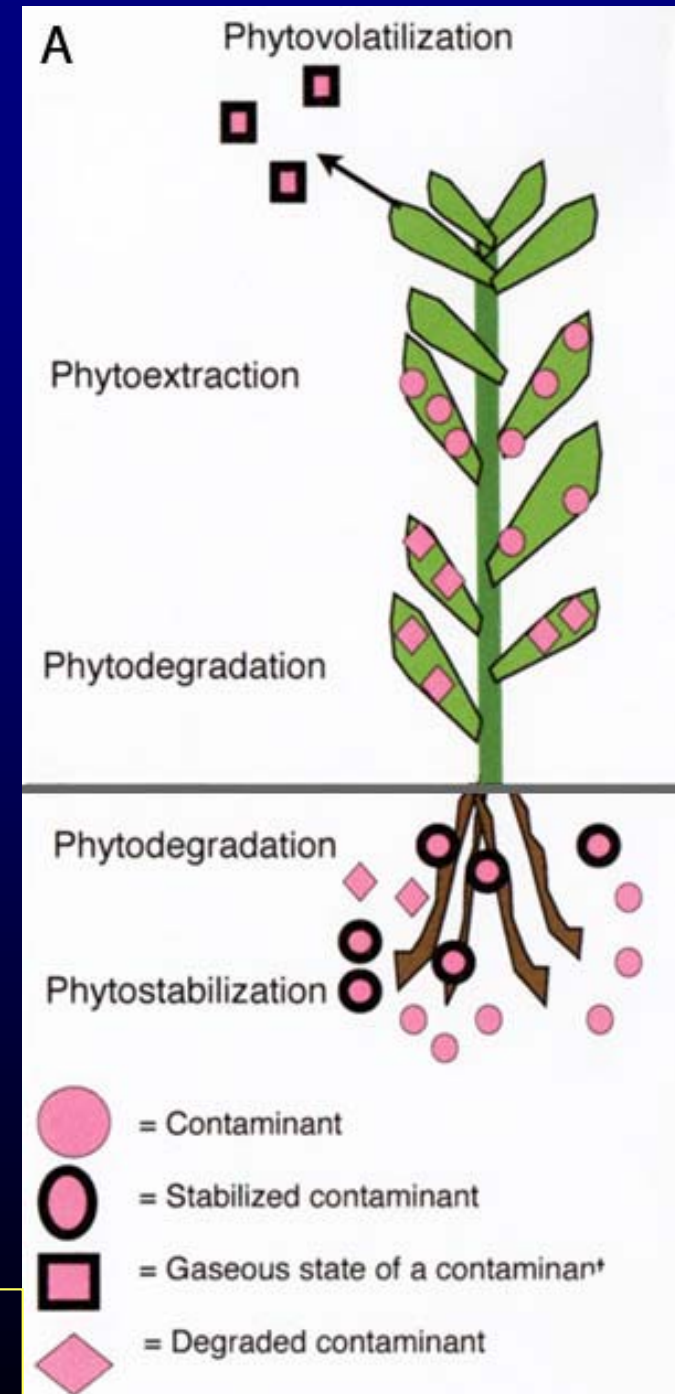
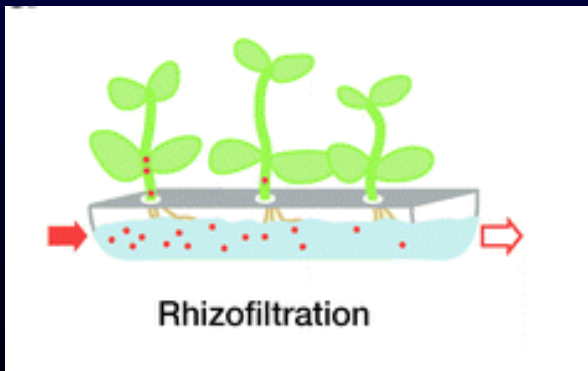
\$5,000 - 8,000



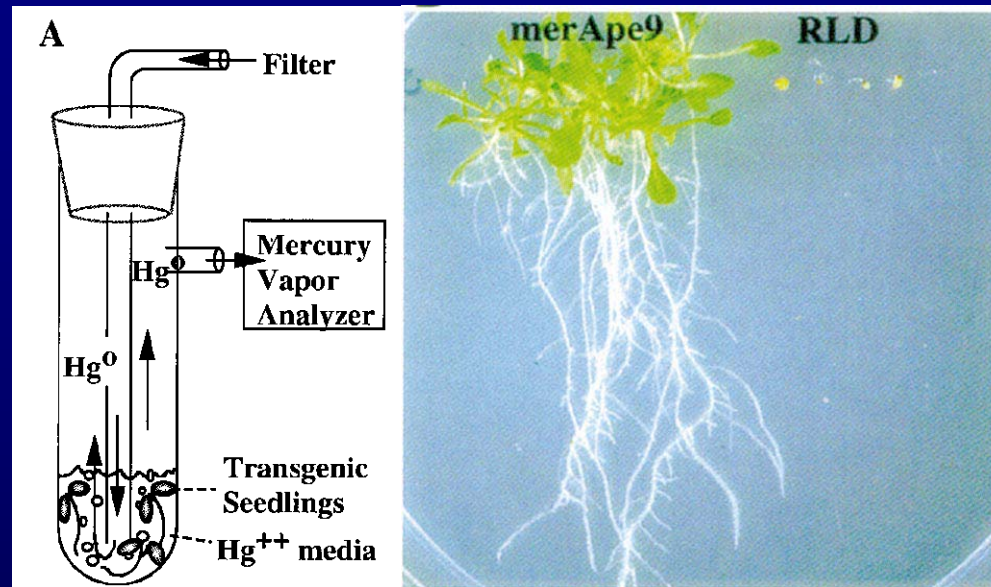
from: <http://urbanomnibus.net/2010/11/from-brownfields-to-greenfields-a-field-guide-to-phytoremediation/>

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



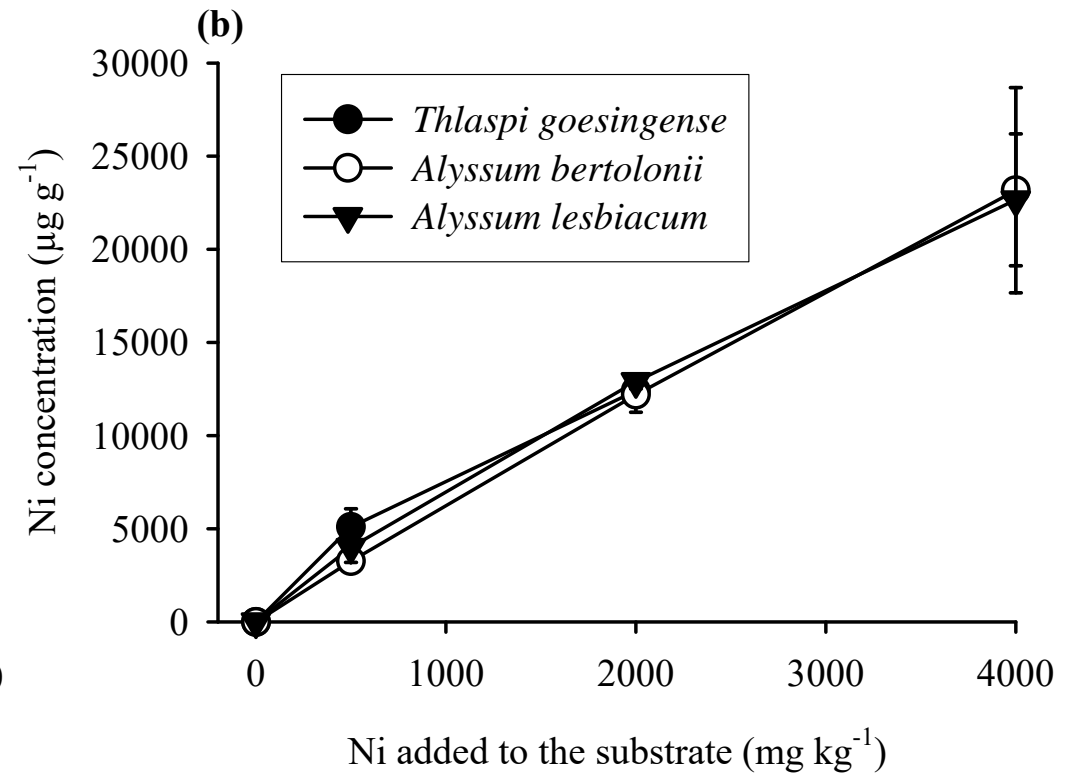
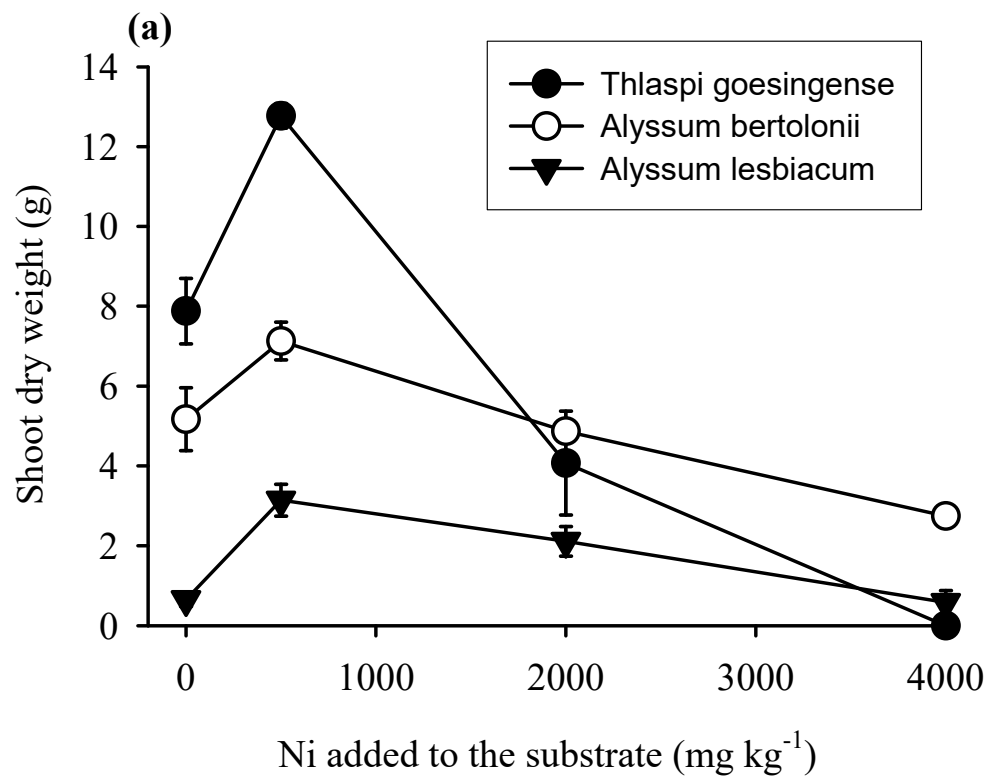
Mercury volatilisation by transgenic plants



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

- Reduction by reductases, e.g. $\text{Hg}^{2+} \rightarrow \text{Hg}_0$
- Not useful for phytoremediation because of re-distribution of pollutant!

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*

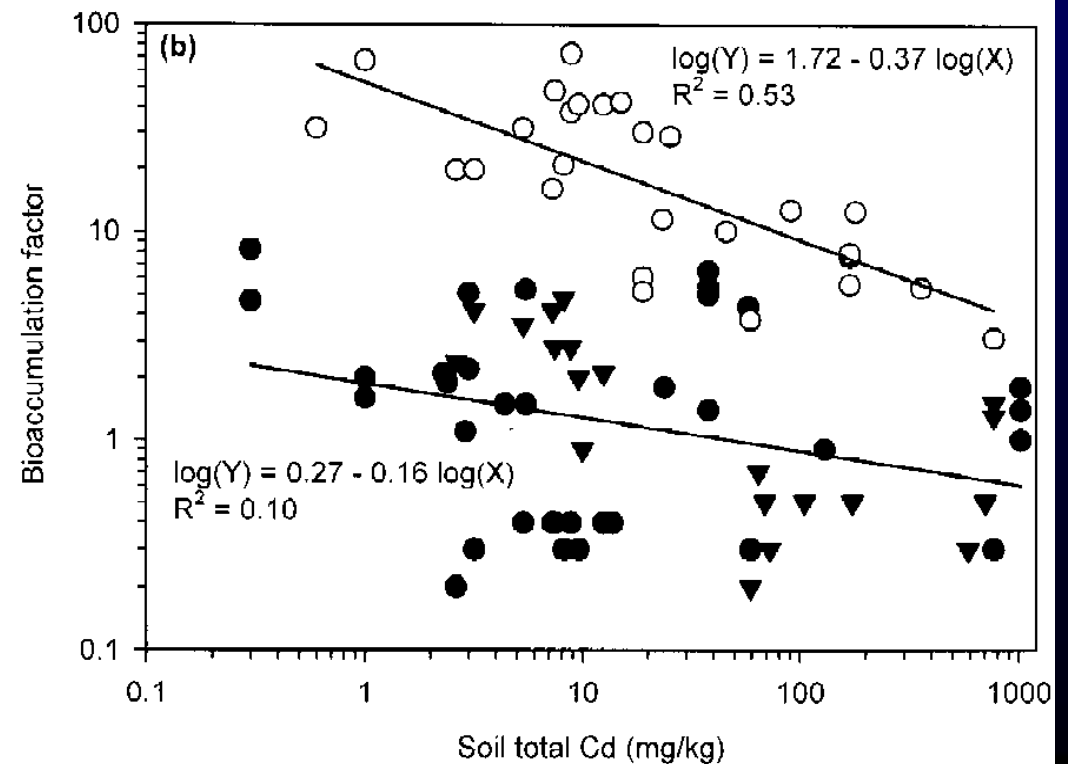
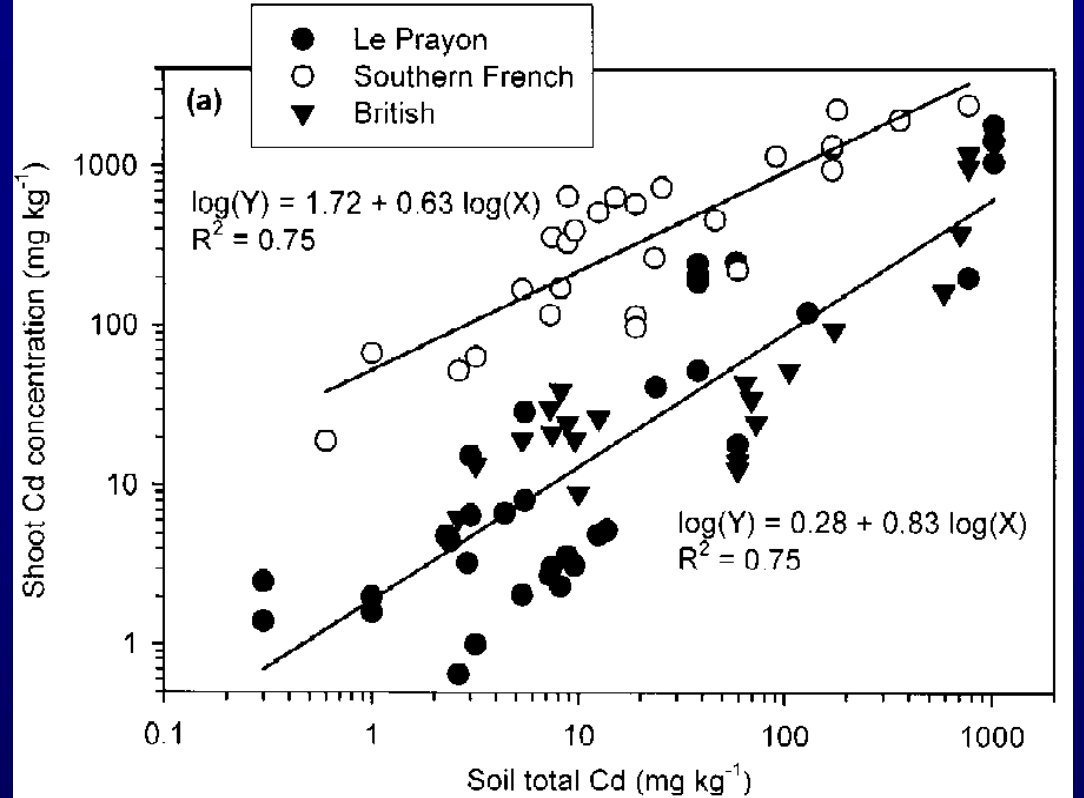


With 10 μM cadmium in the nutrient solution
--> healthy plants

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

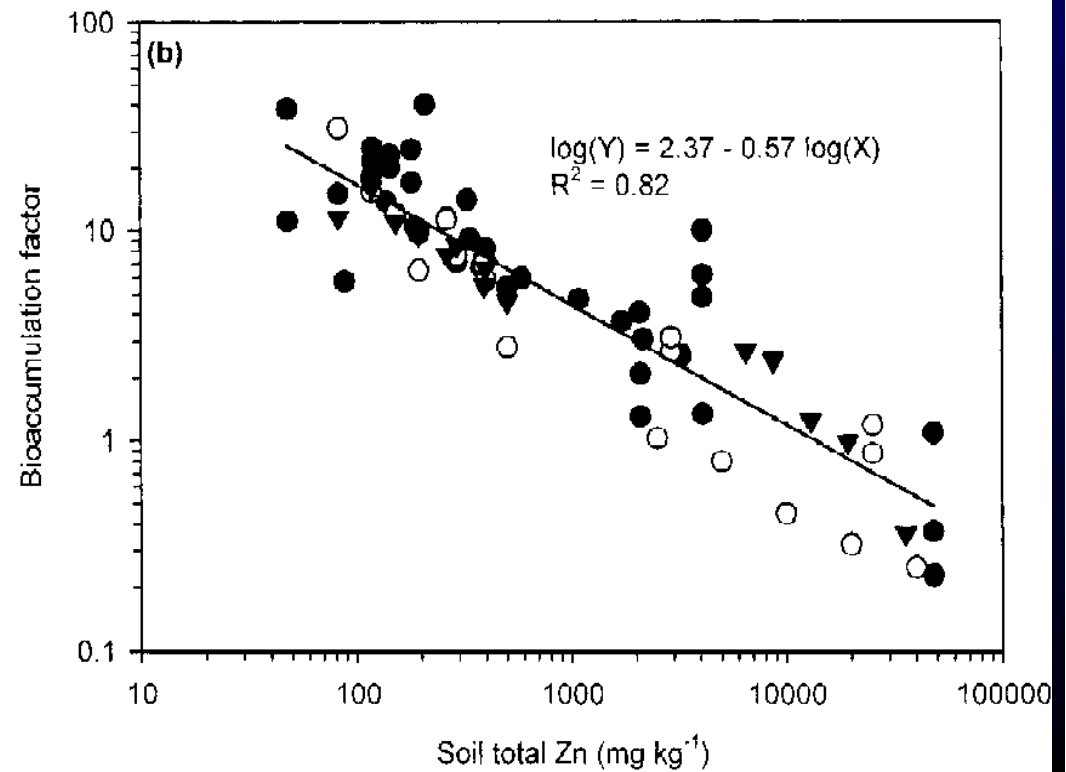
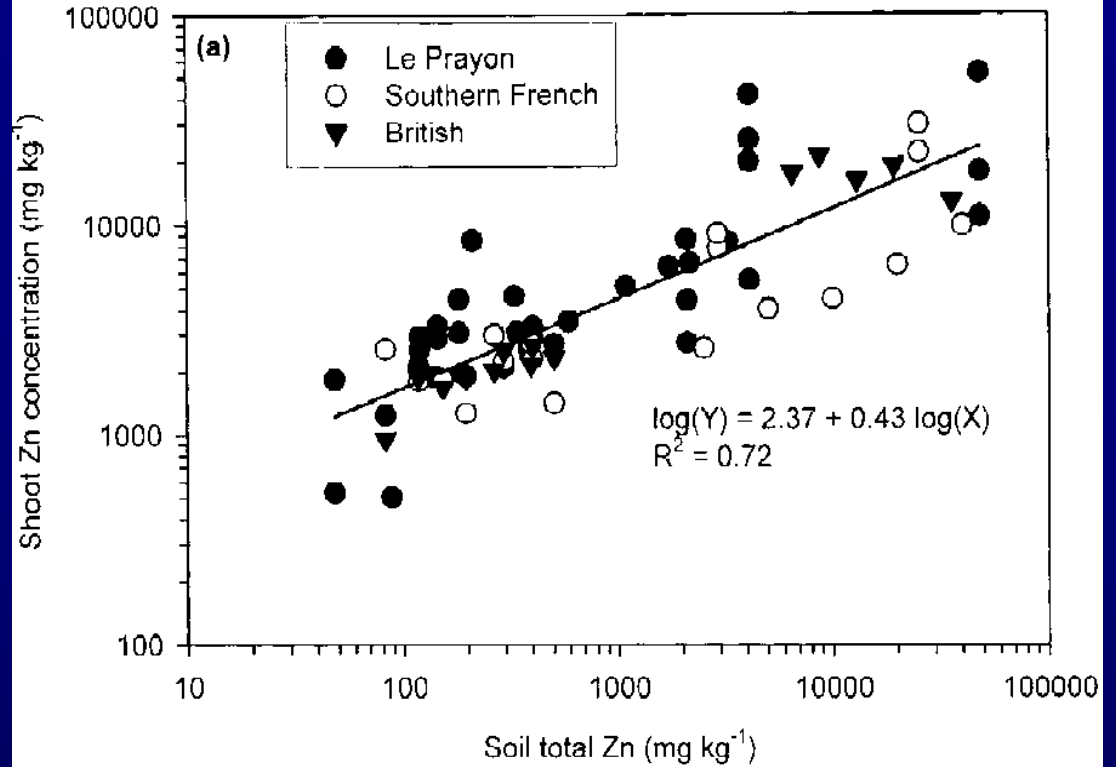
Accumulation of metals in CdZn-hyperaccumulators

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

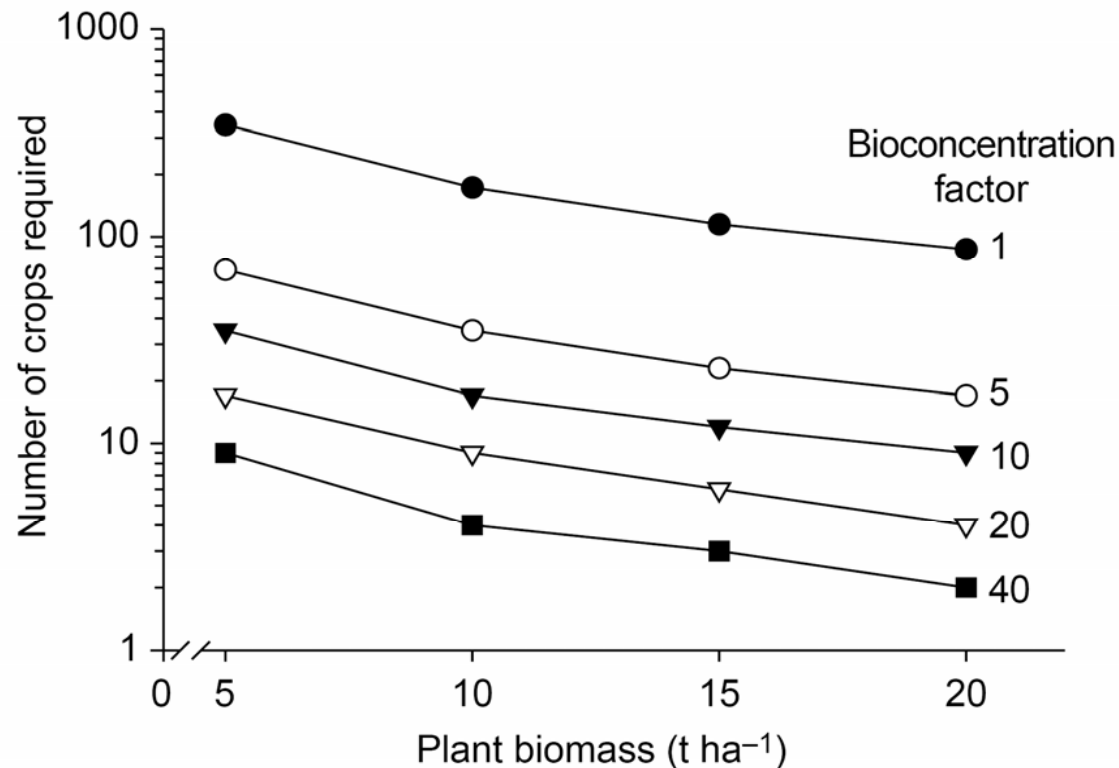


Accumulation of metals in CdZn-hyperaccumulators

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



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.

Phytoremediation with different species

Plant species	Max. Cd mg/kg DW	Biomass t DW/ha	Cd-removal g/(ha*year)
<i>Arabidopsis halleri</i>	100	2	20
<i>Thlaspi caerulescens</i> (Prayon)	250	5	1250
<i>Thlaspi caerulescens</i> (S. France)	2500	5	12500
<i>Dichapetalum gelonoides</i>	2.1	5	10
<i>Athyrium yokosense</i>	165	2	330
<i>Arenaria patula</i>	238	2	476
<i>Sedum alfredii</i>	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]	[mg kg ⁻¹]	Zn in crop [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
<i>Thlaspi</i>	5	25000	125.	3.12	40
Improved <i>Thlaspi</i>	10	25000	250.	6.25	40

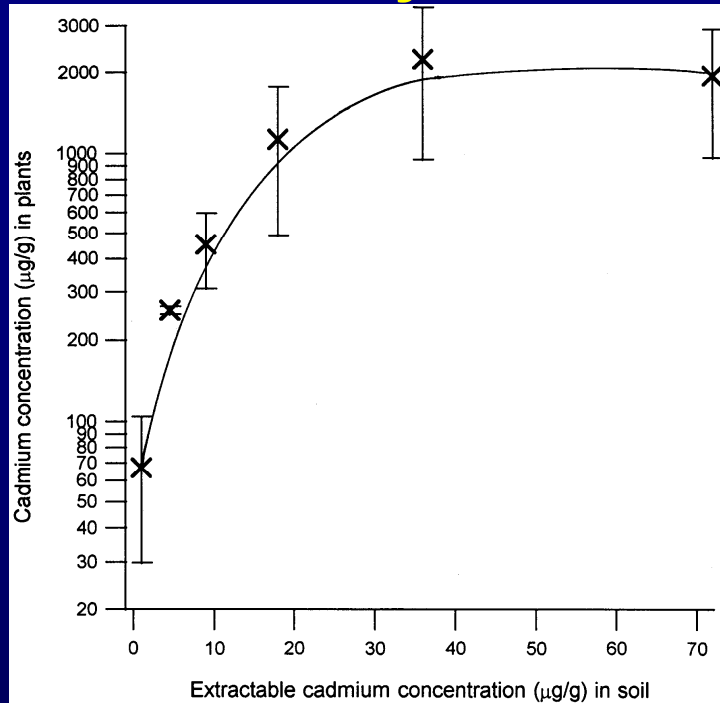
Cd: Presume soil has 20 ppm Cd = 40 kg Cd (ha-15 cm)⁻¹

Crop	Yield [t ha ⁻¹]	[mg kg ⁻¹]	Cd in crop [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
<i>Thlaspi</i> 'Prayon'	5	200	1.0	2.5	0.40
<i>Thlaspi</i> S. France	5	2000	10.0	25.	4.00
<i>Thlaspi</i> Improved	10	2000	20.0	50.	4.00

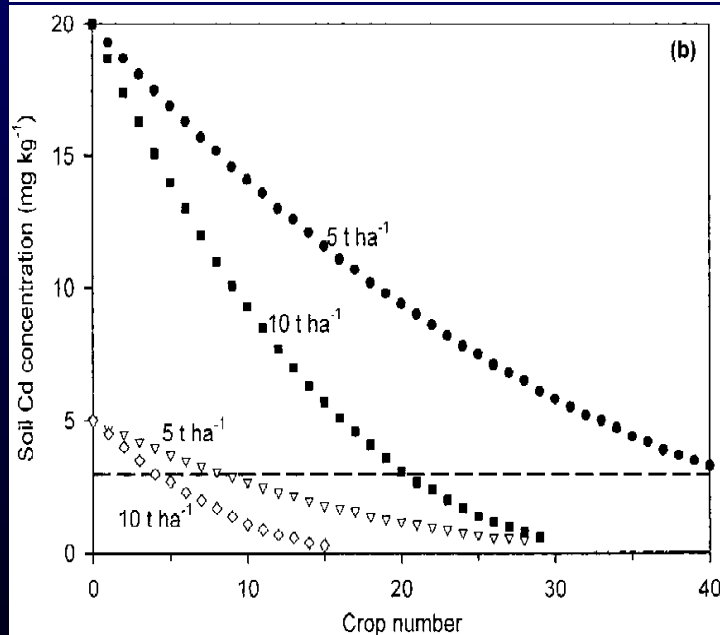
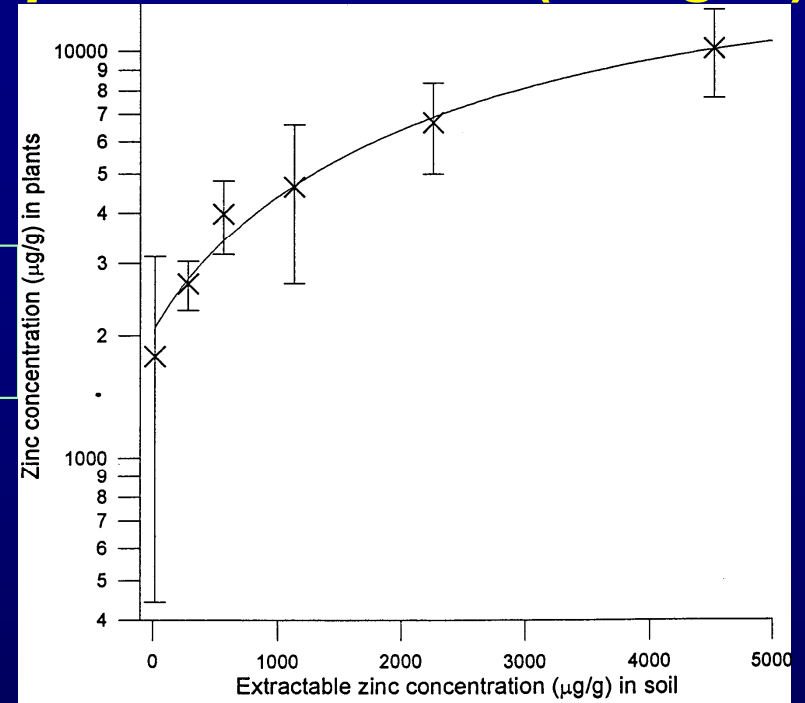


→ Due to its high bioaccumulation coefficient and despite its small biomass, *Thlaspi caerulescens* (Ganges ecotype) is so far the best plant for Cd phytoremediation

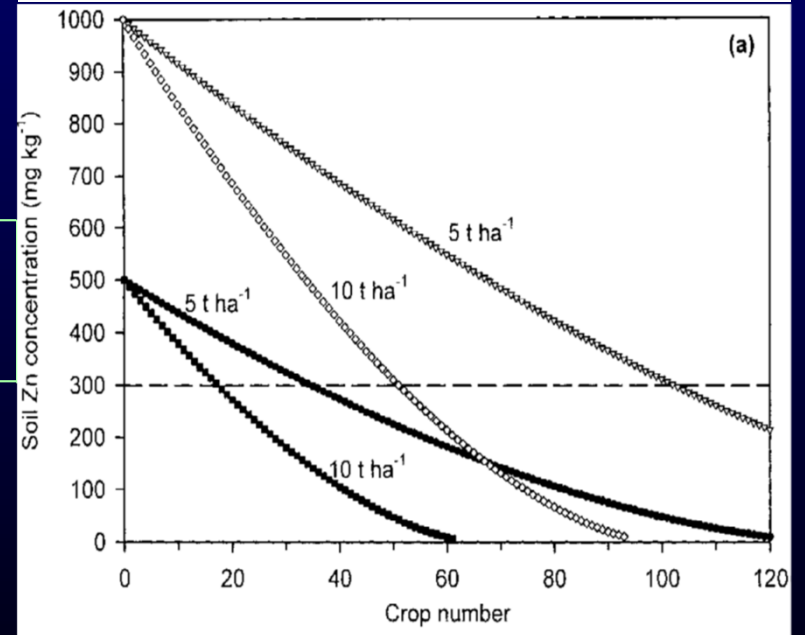
Cd and Zn Phytoremediation with *Thlaspi caerulescens* (Ganges)



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

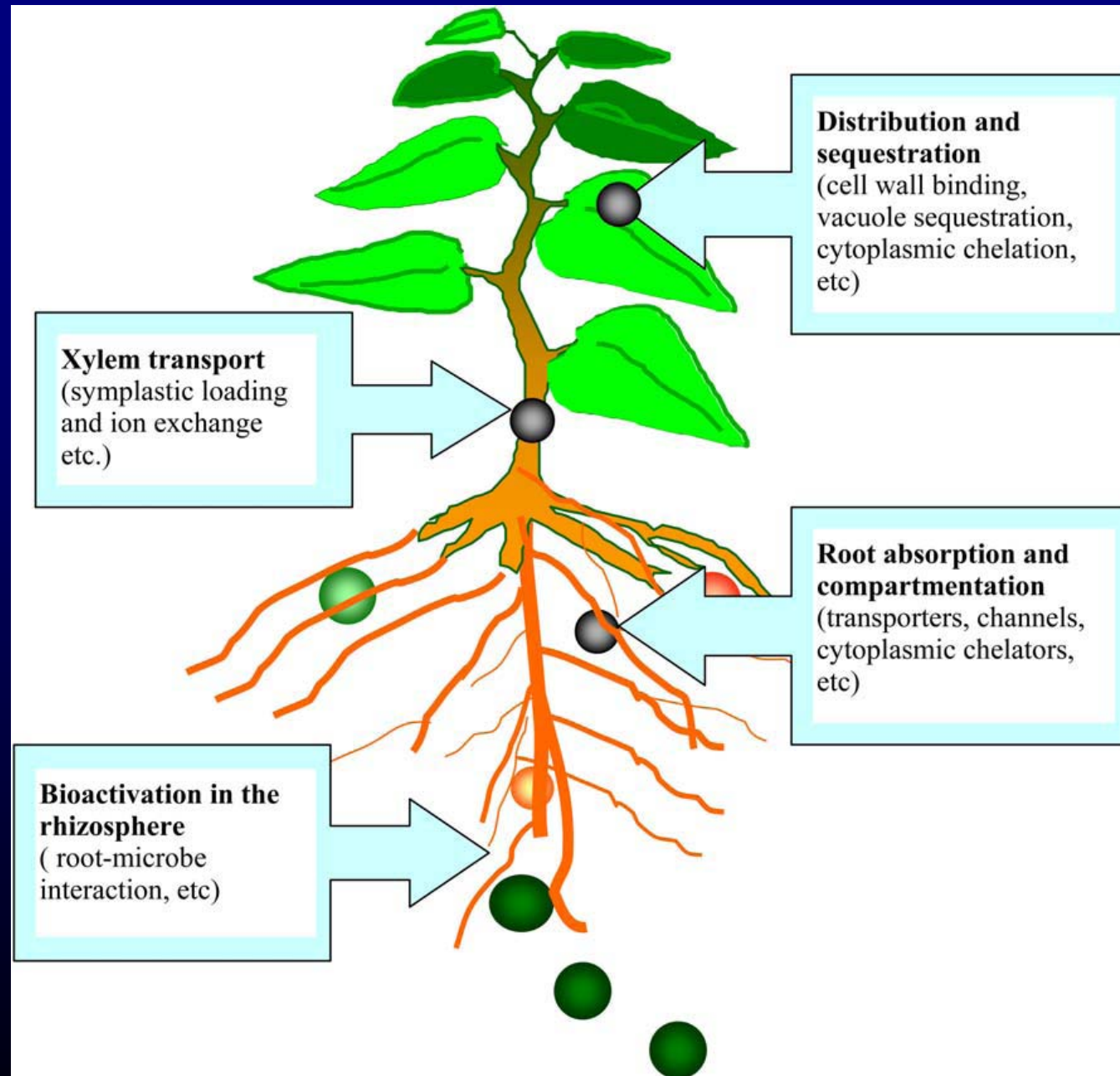


Zhao FJ, Lombi E,
McGrath SP(2003)
Plant&Soil 249: 37-43

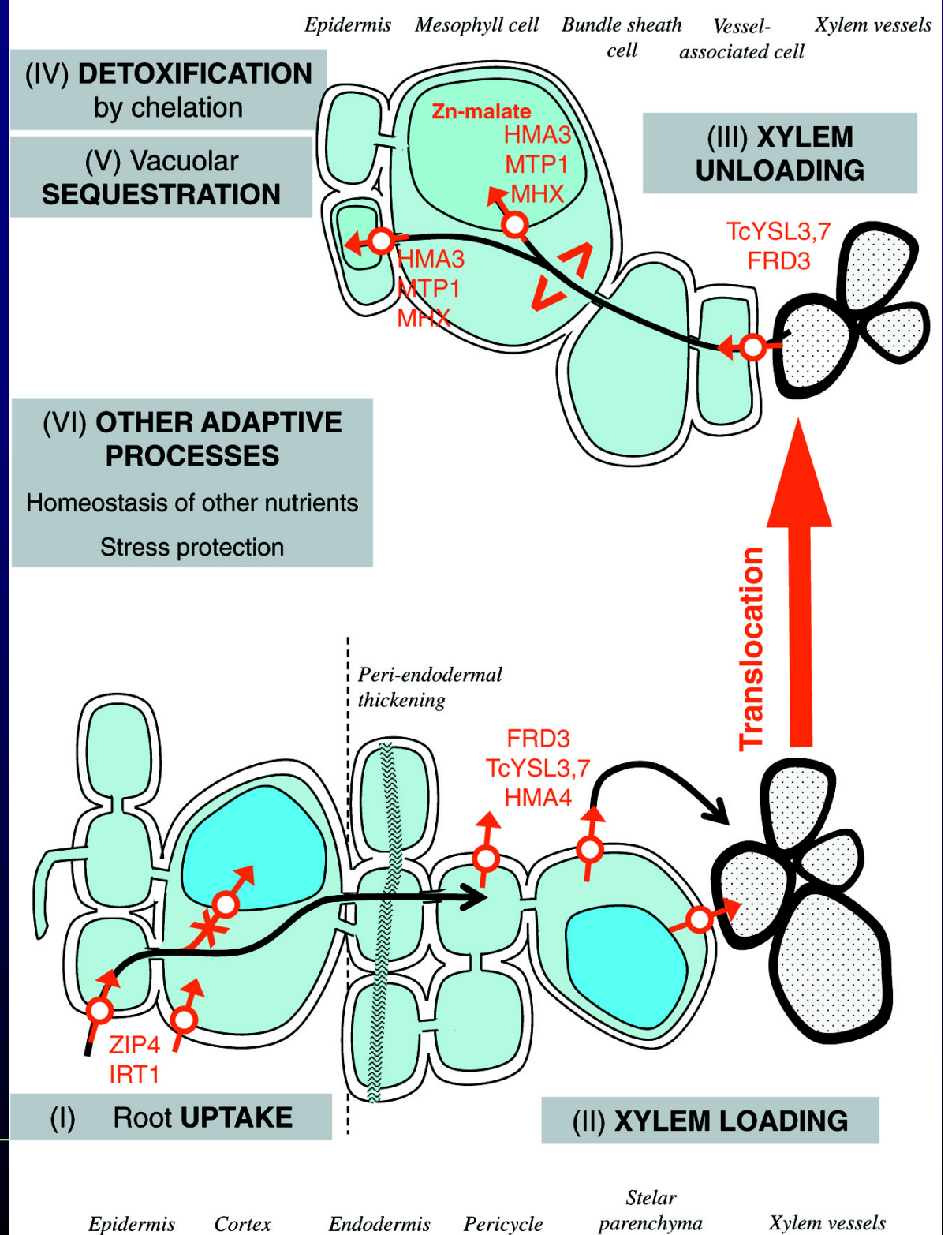


→ While Cd phytoremediation is efficient with *Thlaspi caerulescens*, Zn phytoremediation is inefficient due to lower bioaccumulation coefficient and high soil Zn

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



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



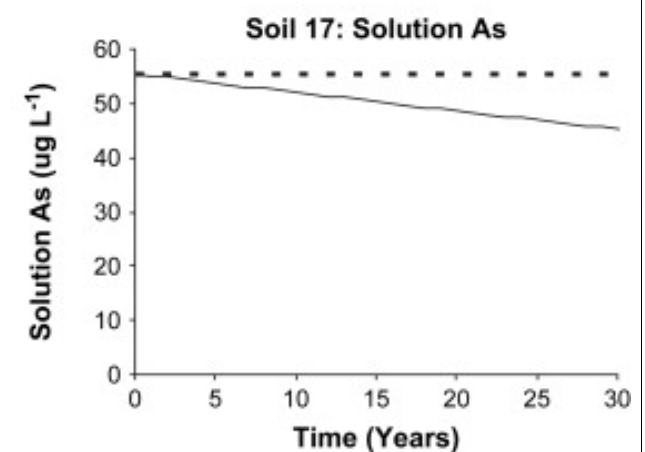
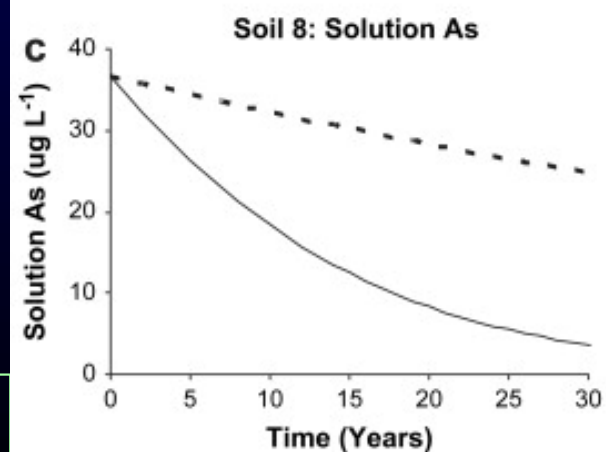
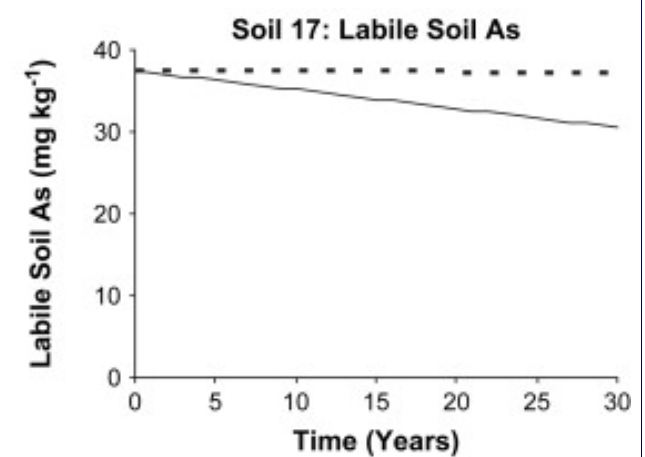
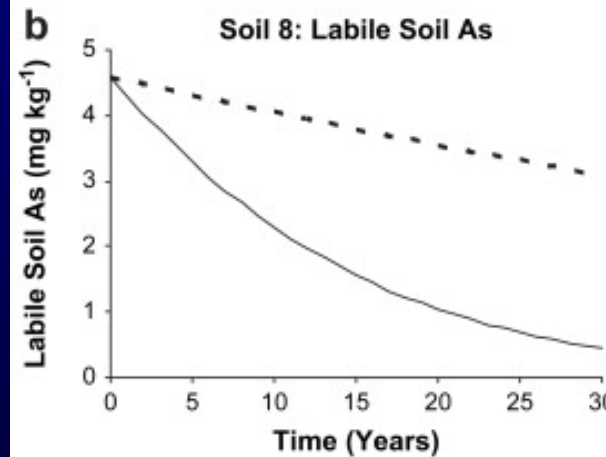
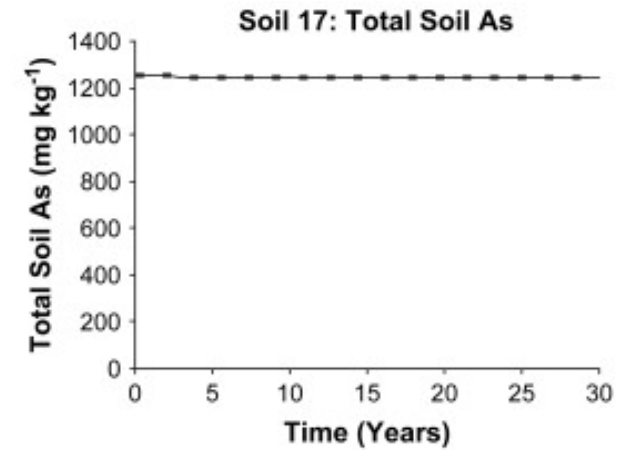
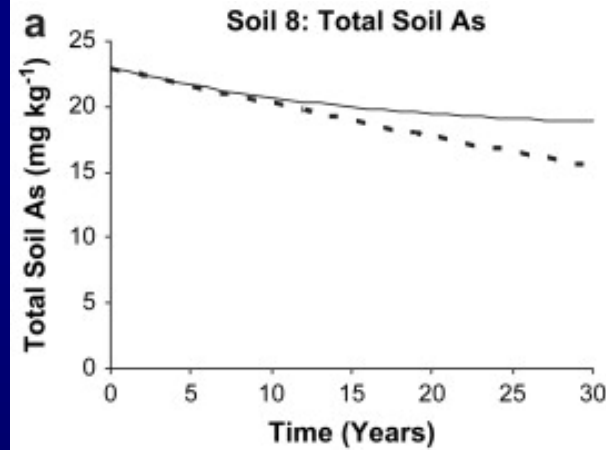
Soil factors influencing phytoremediation – pH and labile metal



→ 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

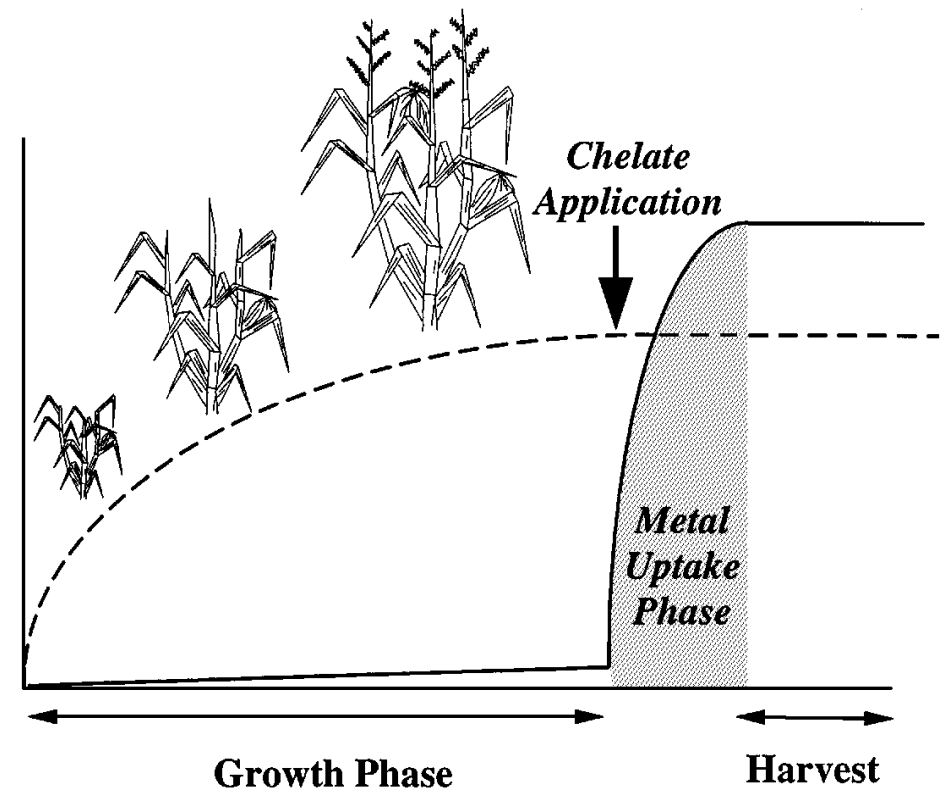
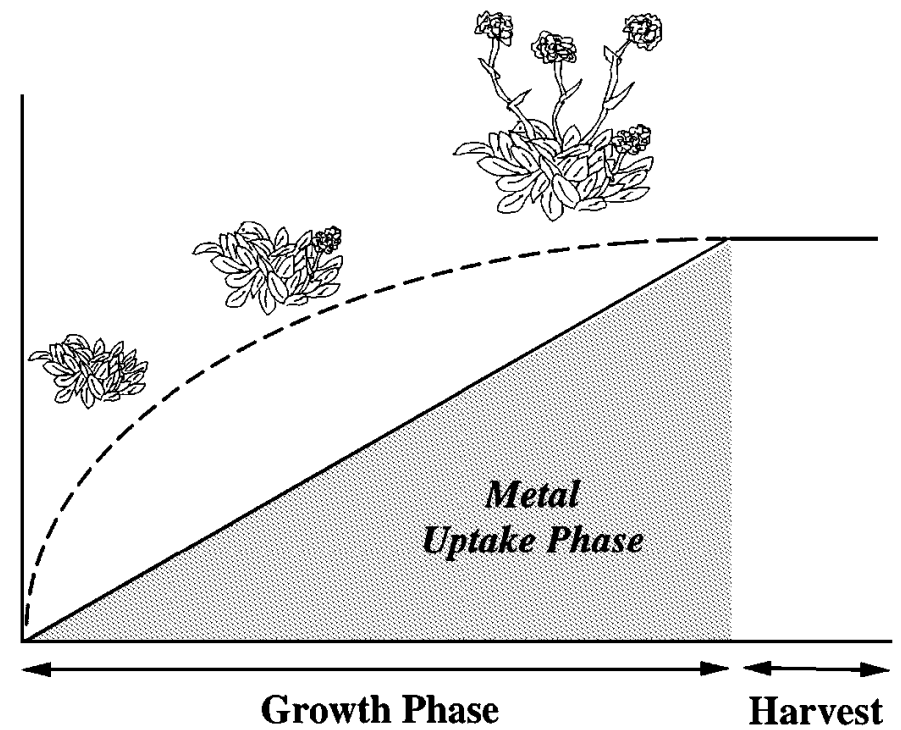
→ detoxification of As works much better in alkaline soils (soil 8: pH 8.1) than in acidic soils (soil 17: pH 5.6)

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



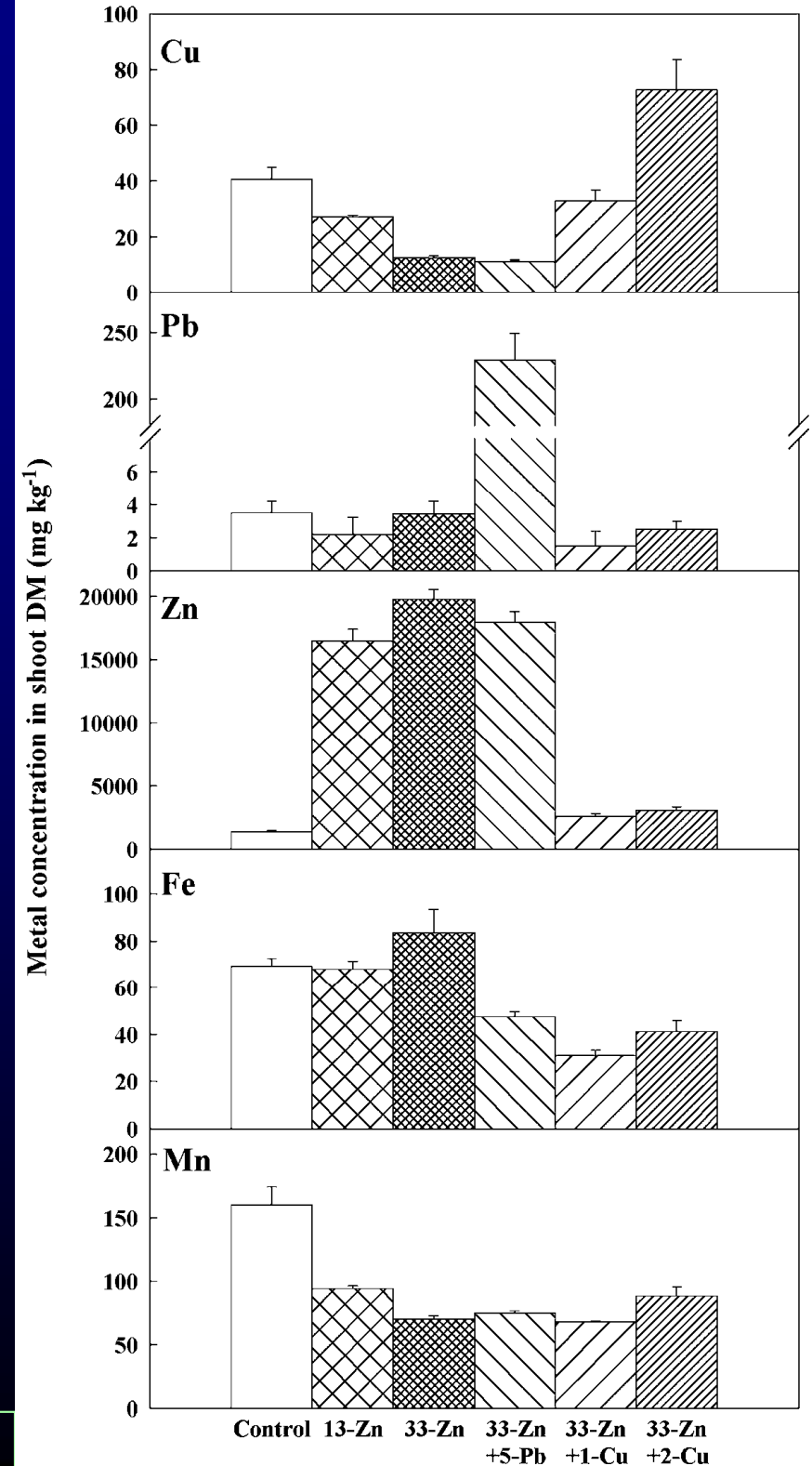
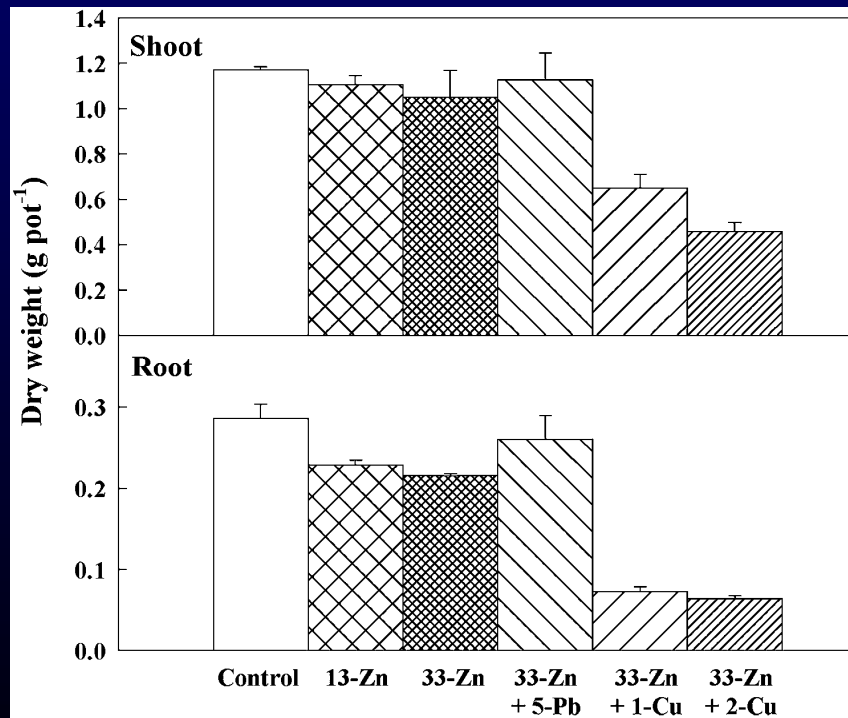
Variants of phytoremediation: continuous vs. chelate-assisted

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



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



Soil factors influencing phytoremediation – toxic metals

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

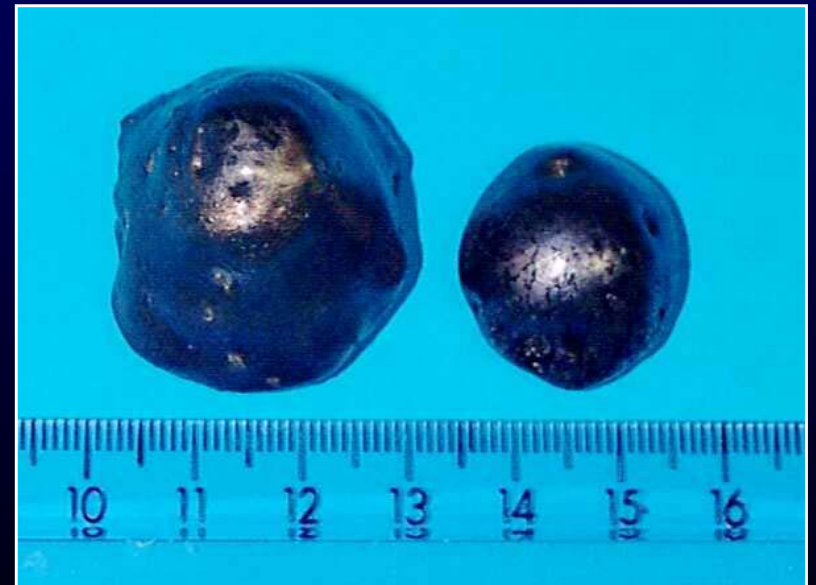


Phytoextraction in action

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



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.

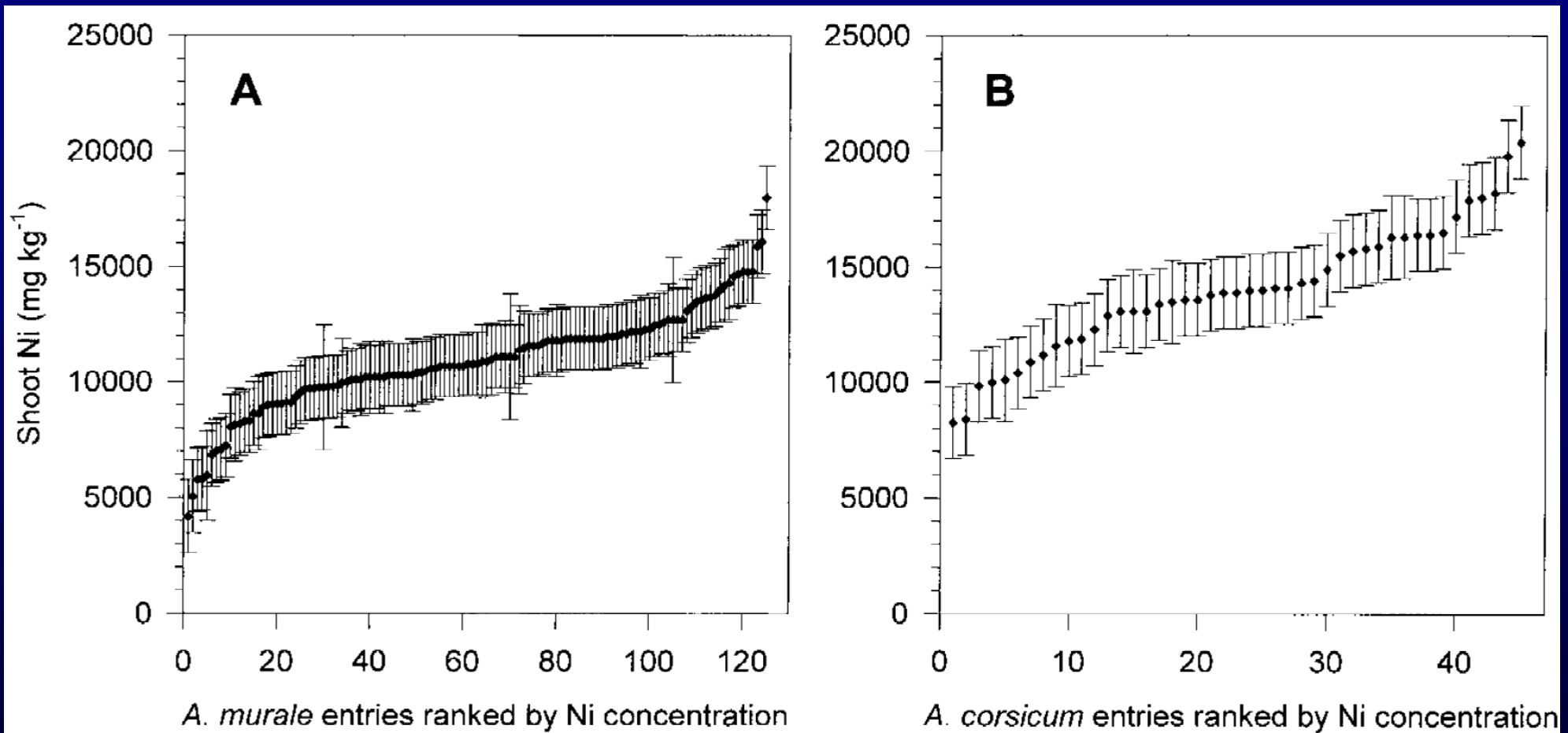
Assume soil contains 2500 mg Ni kg⁻¹ = 10,000 kg Ni (ha-30 cm)⁻¹

Species	Yield [t ha ⁻¹]	[mg kg ⁻¹]	Ni in the crop [kg ha ⁻¹]	(% of soil Ni)	Ash–Ni (%)
Maize (100% normal)	20	2	0.04	0.0004	0.008
Maize (50% normal yield)	10	100	1	0.01	0.20
Wild <i>Alyssum</i>	10	20,000	200	2.0	20–40
<i>Alyssum</i> 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 hectare 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

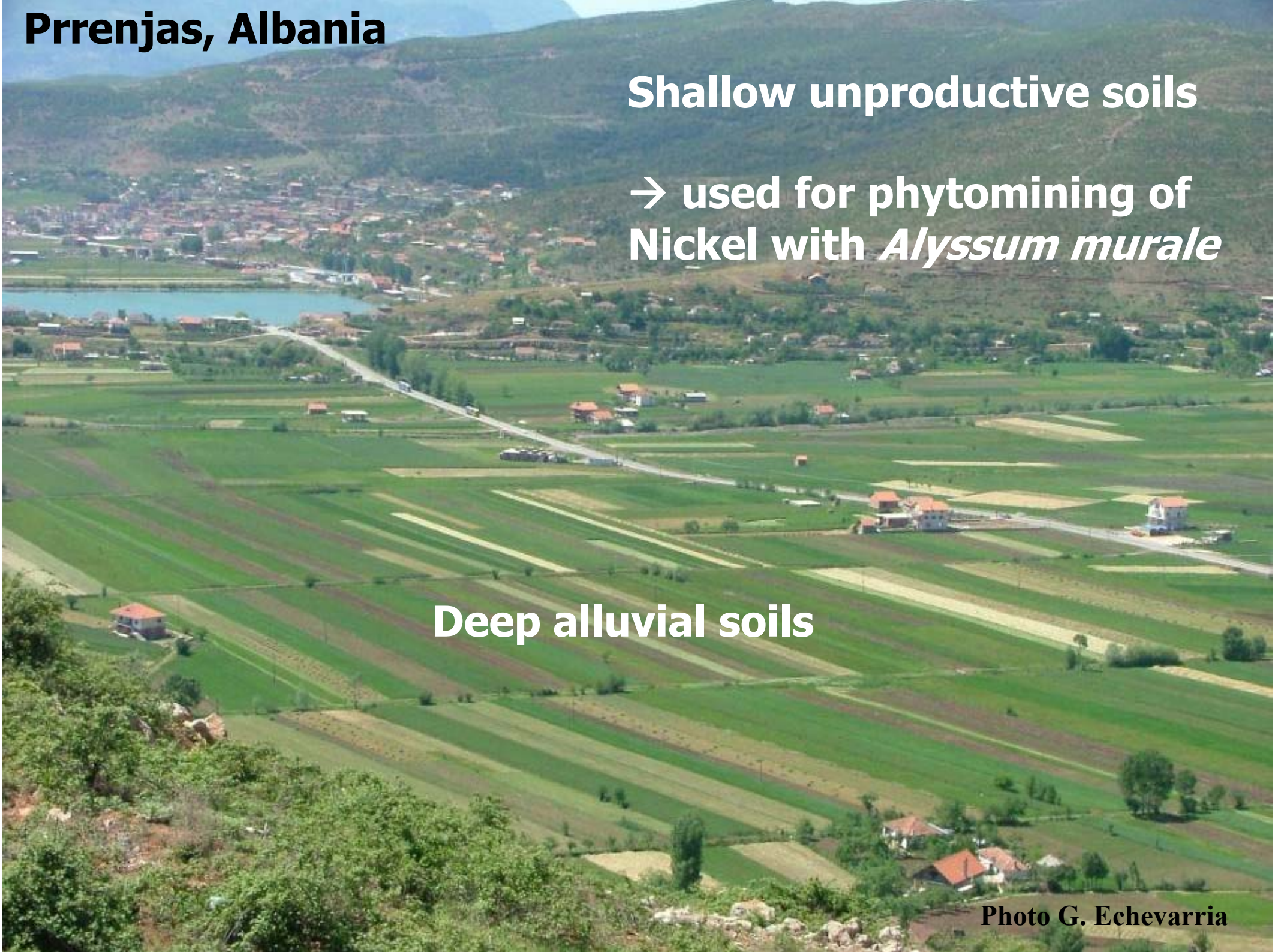
Prrenjas, Albania

Shallow unproductive soils

→ used for phytomining of Nickel with *Alyssum murale*

Deep alluvial soils

Photo G. Echevarria



Prrenjas, Albania

Shallow unproductive soils

→ used for phytomining of Nickel with *Alyssum murale*

Life
AGROMINE



Prrenjas, Pojska, Albania

Shallow unproductive soils

→ used for phytomining of Nickel with *Alyssum murale*

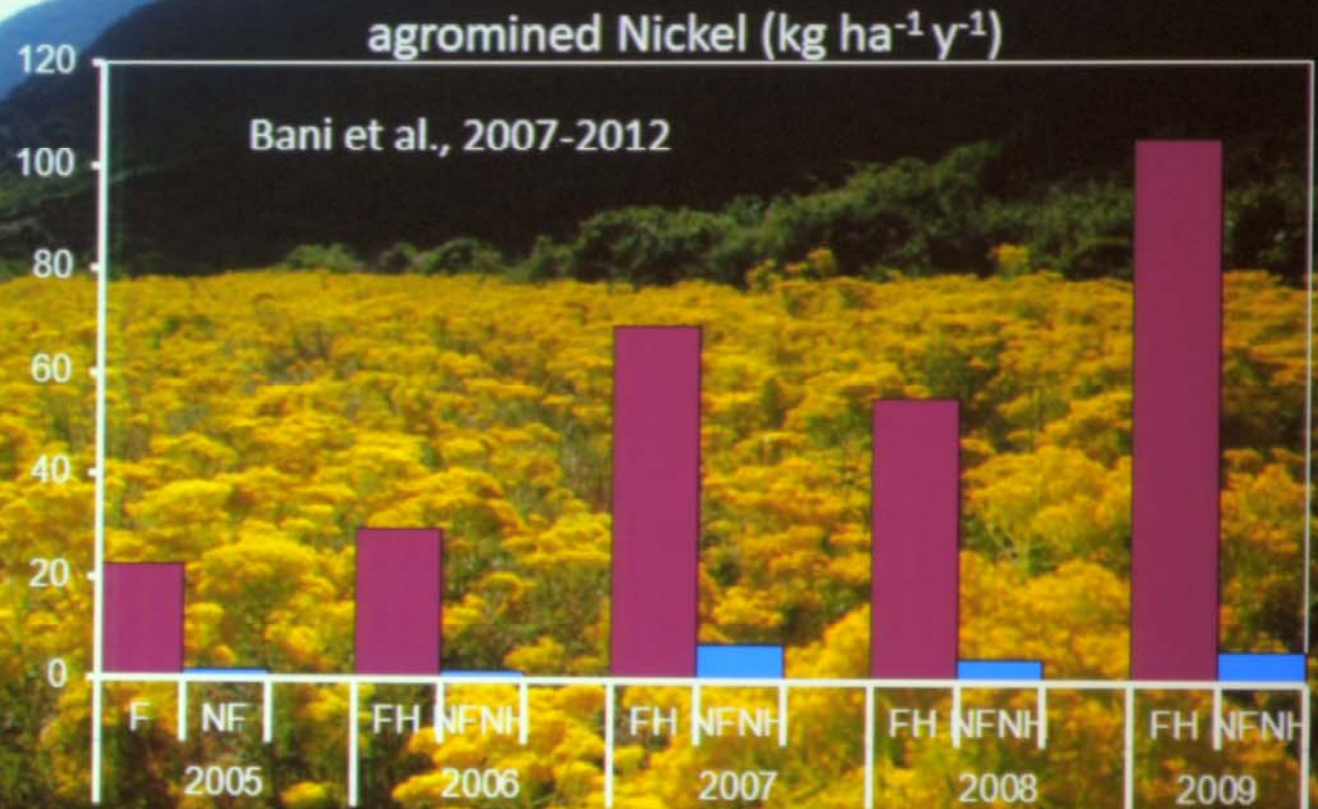


Photo G. Echevarria

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

Phytomining in the tropics

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



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

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

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	<i>Rinorea bengalensis</i>	<i>Phyllanthus rufuschaneyi</i>
Size	30 m tree	3 m shrub
Maximum Ni concentration in leaves	2.7%	6%
Propagation	Seeds	Cuttings

Phytomining in China

Agromining and hydrometallurgy of REEs using *Dicranopteris linearis*

Dicranopteris linearis



(Liu WS et al. Plant Soil, 2019)

- A REEs accumulator, up to 0.3% REEs in shoots.
- 0.2 wt% Al and high levels of Si in shoots.
- Potential for phytomining on REEs- and Al-stressed soils.

REE/Al detoxification



cf. Oral - Liu Wenshen-S10-10

REE agromining



(Chour et al., Chem. Eng. Process., 2018)

D. linearis

Aqueous extraction

REE³⁺
REE complex

Selective adsorption

REE³⁺
+ impurities

Selective elution

REE³⁺

approach #2A

Selective precipitation

REE oxalates

Calcination

REE oxides

approach #2B

> 300

Concentration factor
plant – final solid

> 70%

Recovery of REEs

One big mining company currently employing phytomining

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

The screenshot shows the Inco website's Environmental, Health and Safety Report for 2002. The page features a navigation menu on the left with categories like Executive Summary, Health & Safety, and Performance Profiles. The main content area is titled 'Performance Profiles' and 'Phytomining'. It includes a photo of a woman in a hard hat, a photo of Dr. Bruce Conard, and a photo of a green plant. The text describes the use of *Alyssum* plants for phytomining in Indonesia.

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

Home : Glossary : Search : Site Map : Contact Us

2002

Environmental, Health and Safety Report

Print This Page

Home > Performance Profiles > Phytomining

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.

Back to Top

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Last Updated: Friday, March 30, 2012

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

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

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

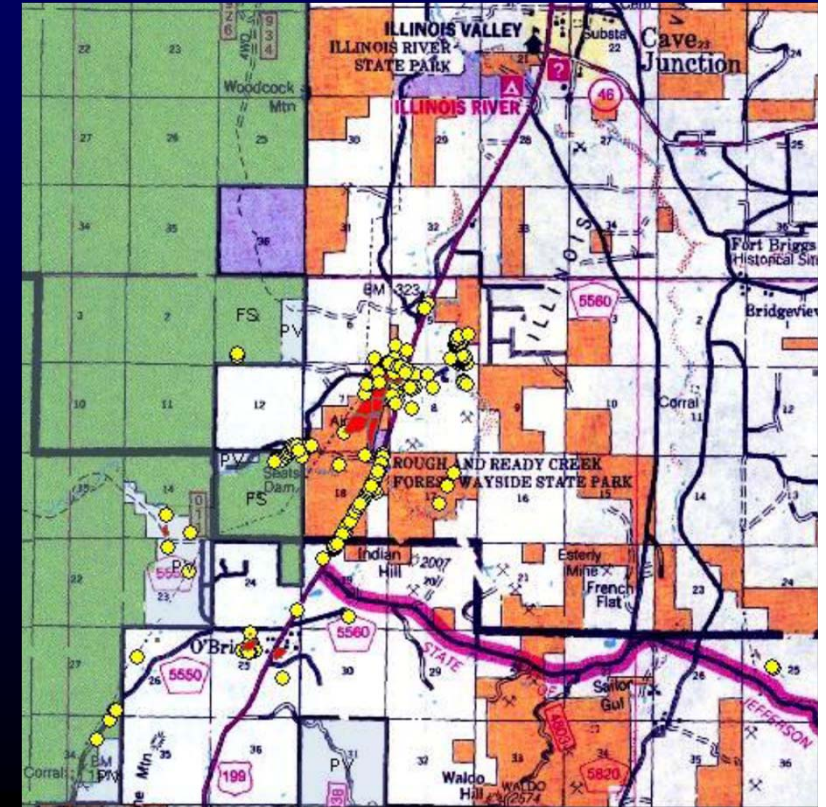
<http://www.co.josephine.or.us/Files/AlyssumStory.pdf>

- 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



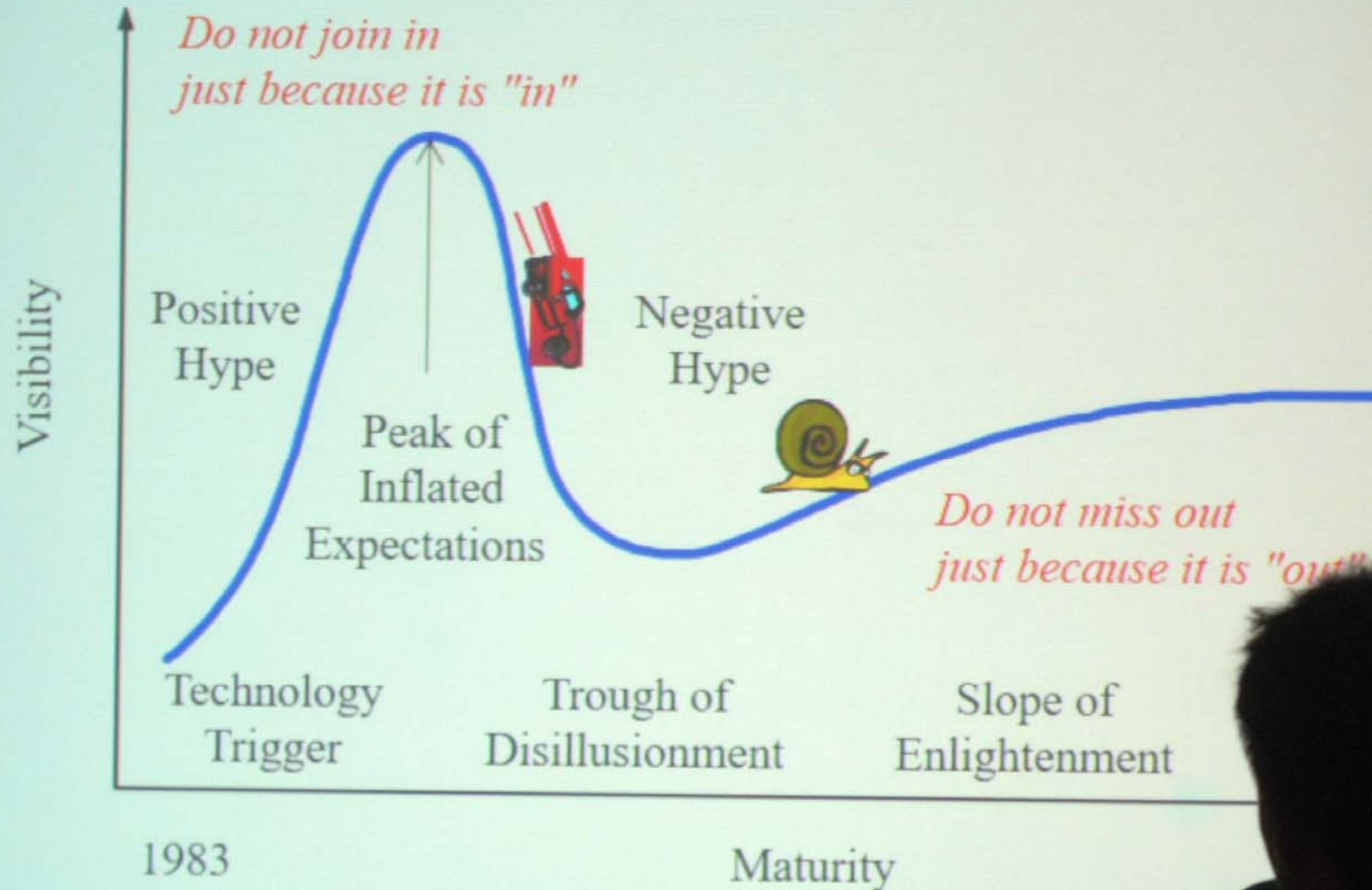
red: planted sites
(2002)

yellow: escaped
sites (2010)



Summary

Quo Vadis Phytotechnologies?



**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