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/

Hendrik Küpper, Advanced Course on Bioinorganic Chemistry & Biophysics of Plants, summer semester 2019
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

Phytoextraction

$50,000 - 100,000

$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

- Reduction by reductases, e.g. $\text{Hg}^{2+} \rightarrow \text{Hg}_0$, $\text{Cu}^{2+} \rightarrow \text{Cu}^{+}$

Rugh CL, et al, 1996, PNAS 93, 3182-3187
Plants with an unusual appetite: Heavy metal hyperaccumulation

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

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!

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

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

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

Z Naturforsch 60c, 190-8

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)

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)

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

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
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“.

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.

<table>
<thead>
<tr>
<th>Species</th>
<th>Yield [t ha⁻¹]</th>
<th>Ni in the crop [kg ha⁻¹]</th>
<th>Ash–Ni (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maize (100% normal)</td>
<td>20</td>
<td>2</td>
<td>0.0004</td>
</tr>
<tr>
<td>Maize (50% normal yield)</td>
<td>10</td>
<td>100</td>
<td>0.01</td>
</tr>
<tr>
<td>Wild <em>Alyssum</em></td>
<td>10</td>
<td>20,000</td>
<td>2.0</td>
</tr>
<tr>
<td><em>Alyssum</em> cultivar</td>
<td>20</td>
<td>30,000</td>
<td>6.0</td>
</tr>
</tbody>
</table>

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


→ large variation in metal accumulation between populations of hyperaccumulator species allows for efficient selection of high-yield ecotypes
One mining company currently employing 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 phytoremediation. There are two applications of phytoremediation:
- 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 baked and harvested, like hay, and then burned in an incinerator. The metal content of the resulting ash is superior to commercial mixed ore and the metal in the ash can be recovered using conventional metal processing technology. The heat created by burning the ash can also be used to generate power.

We have been cooperating with Alyssum crops with Visionaire Resources LLC of Houston, Texas. The advantages of phytoremediation 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, "mineral farming" could continue for centuries.

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

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...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)
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