# Phytoremediation

## A broad topic at the intersection of chemistry and plant and environment science

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  can be fought, and how ?
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# Choice of topic

Suggested by an article on **phytomining** by the New-York Times
[https://archive.ph/P2sSl](https://archive.ph/P2sSl)

In Malaysia, plants were being used to suck nickel out from the soil in abandoned mining plots. The **metal** is then **collected**, either by burning or squeezing the cut plant.

If metal can be extracted from the soil instead of the rock, while not disturbing but rather improving the environment, **what else** is possible ?

The New York Times

*Down on the Farm That Harvests Metal From Plants*

Hyper-accumulating plants thrive in metallic soil that kills other vegetation, and botanists are testing the potential of phytomining.

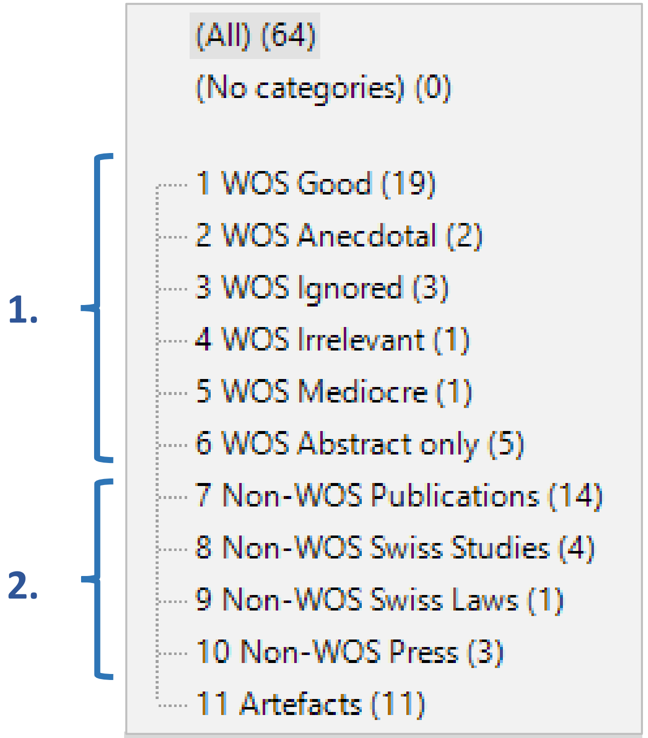
# Literature search

1. Web of Science

- Terms “**phytoremediation** (Topic) AND **review** (Abstract)”
- Obtained 1092 results
- Selected the top 100
- Selected 31 after reading the abstracts
- Rated them from 1 to 5

2. Other

- 18 additional articles
- 4 other references
- Grouped by type




Rating references using Citavi categories

# Definitions

1. The use of plants to remove pollution from the environment.
2. The use of appropriate plants (hyperaccumulators) and associated agents (fungi, bacteria, hormones…) to remove pollutants from the environment.
3. The removal, using plant systems, of toxic substances from the environment by transport, detoxification/degradation, containment or a combination thereof.

# History and scope

Three phases seem to stand out in the selected literature

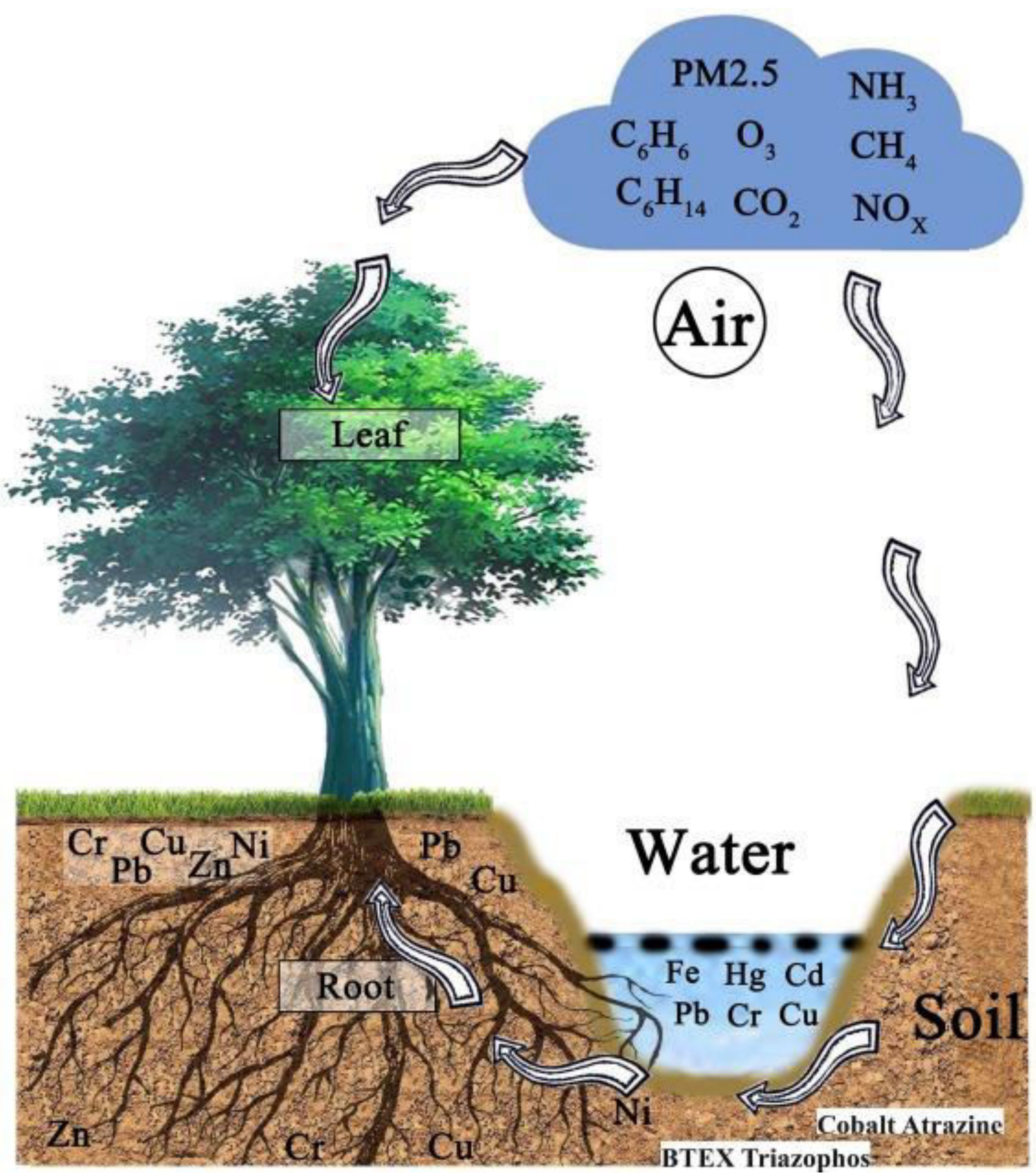
- 1990s development of the fundamental principles (how well does it work?)
- 2000s models, more varied use cases (where and when does it work ?)
- 2010s supportive techniques (how to make it work better ?)

- Phytoremediation covers multiple domains and techniques, the histories of which are intertwined.
- For phytosanitation, a ready-to-go system consisting of tilted-bottom ponds by Dr Reinhold Kickuth was available in the 1970s.

# Advantages

**Traditional methods** to remove pollutants, including earth relocation and heat, chemical or biological treatment are **expensive** and **destructive**. In comparison, phytoremediation techniques:

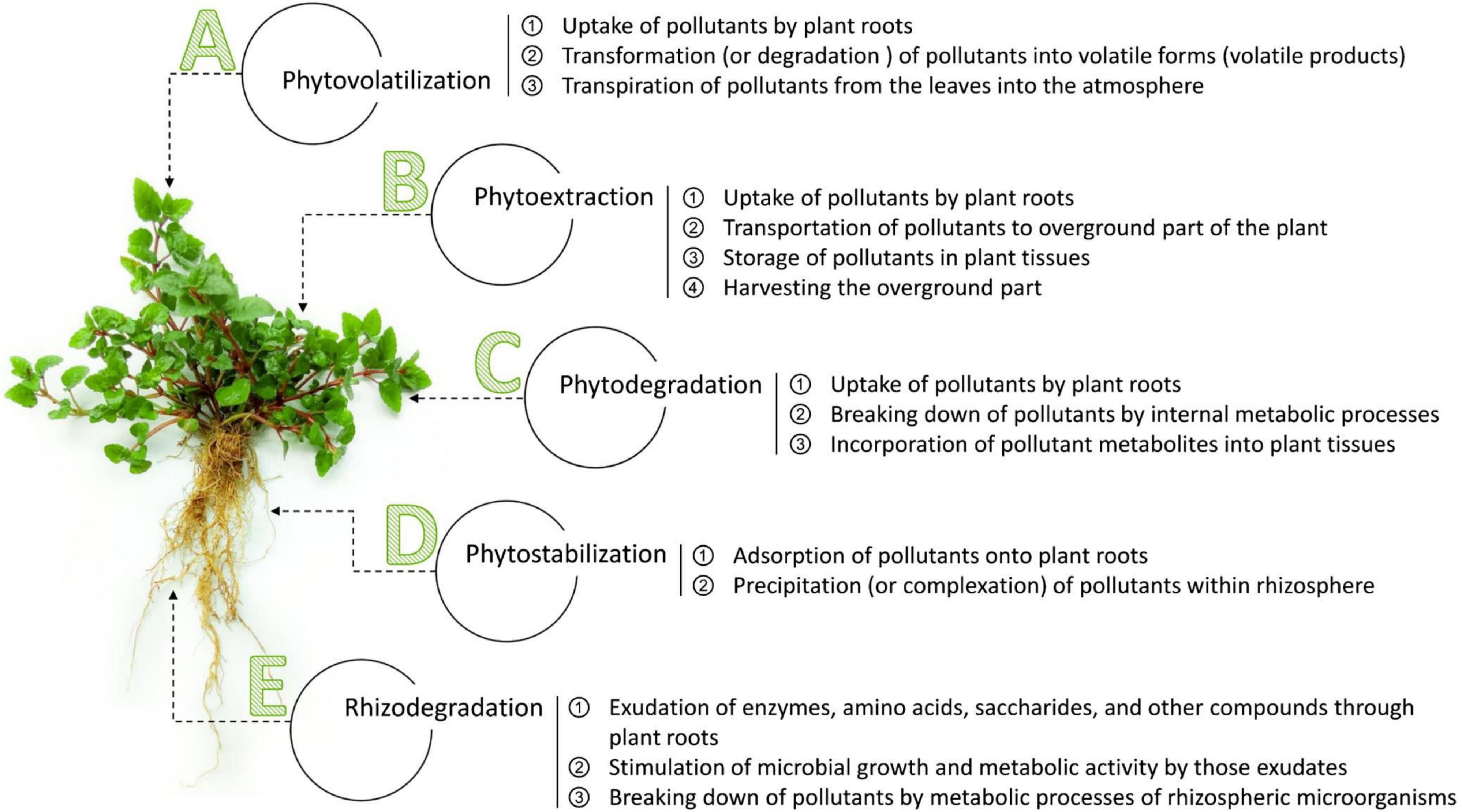
- Rely on self-sustained processes
- Improve soil characteristics
- Require modest logistics
- Require little maintenance
- Incur no energy cost
- Can be aesthetically pleasing




# Applicability domains

A schematic drawing showing phytoremediation in air (particulate matter and volatile organic compounds), soil (heavy metals) and water (heavy metals and organic matter). (Wei et al., 2021)

# Phytoremediation can rely on several mechanisms




Phytoremediation technologies for abating soil pollution. (Song et al., 2019)

# What to do after extraction or degradation ?

- Once the accumulation process has taken place, standing biomass must be **removed from the site** and “disposed of”.
- Composting reduces volume and further increases metal solubility.
- Heat generation, where applicable, is another productive way of disposal.
- The remaining material is **bio-ore**, very rich in metals.
- Energy production profits make ore extraction more viable.

High nickel content (green) in
*Pycnandra acuminata*’s sap
[Antony van der Ent; www.br.de]

Q1. For which kinds of pollutions is phytoremediation applicable ?

# Phytoremediation in soils

- **Heavy metals** (As, Cu, Cd, Cr, Pb, Hg, Se, Ni, Zn) are the most common pollutants.
- The root zone provides “the entry points into metabolic pathways” (Yadav et al., 2018)
- “the amount of contaminant plants can accumulate increases with their biomass [and] the surface area of their root systems” (Yang et al., 2020)
- Certain plants are called **hyperaccumulators**; “these plants have an innate capacity to **absorb metal at 100 times greater than average** plants” (Yadav et al., 2018)
- The *Brassicaceae* family contains several metal hyper-accumulators: *Brassica* (mustard), *Thlaspi, Arabidopsis*...

*Barbarea vulgaris*
[H. Zell]

# Essential and non-essential metals and metalloids

**Essential**

Cu

Fe

Mn

Ni

Zn

- "Some metals are required by plants as essential micronutrients for proper plant growth."
- "Heavy metals enter into the agro–ecosystem by natural as well as anthropogenic processes."
- "heavy metals in agricultural soils and water resources poses a great threat to human health"
- (Sarwar et al., 2017)

**Non-essential**

As

Cr

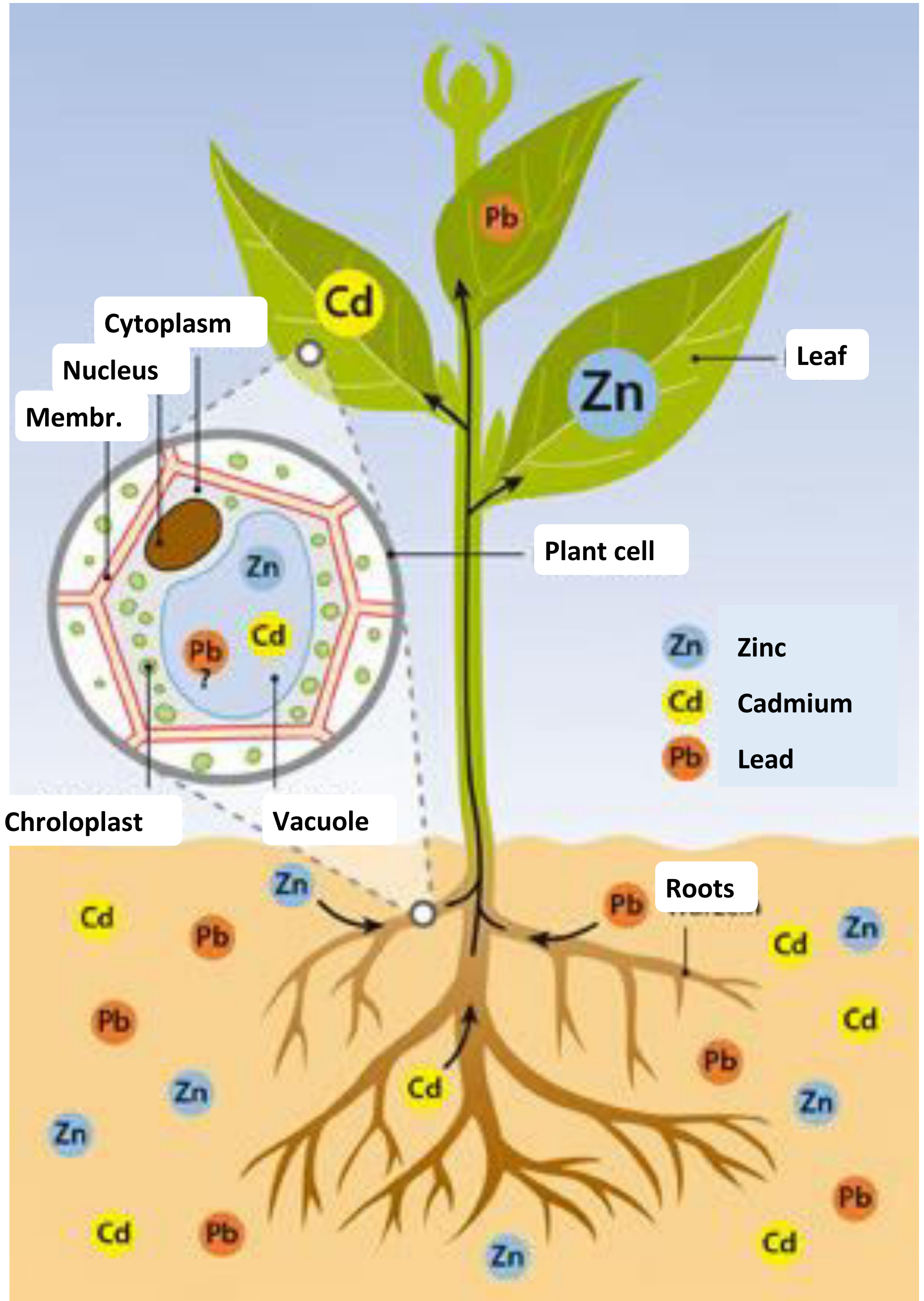
Ag

Cd

Pb

Se

Hg



Adapted from [Deutschlandfunk Nova]

# Where do the metals go ?

- There are four places where the plant can store heavy metals from the soil: on the root (adsorption), in the root (absorption), in the shoot (can be cut down), in the leaf (some can be volatilized)
- Inside the plant, heavy metals are transported in the xylem; they can enter the cell and be stored in the **vacuole**.
- This is permitted by the chelation of free metal ions by ligands such as amino acids.
- Different pollutants cause the accumulation of different amino acids. (Yan et al., 2020)

# **Topsoil conditions** are a determining factor

- The pollutant mix has an effect on the plant uptake of each pollutant “the interaction between pollutants must be considered when judging the phytoremediation of multiple pollutants” (Yang el al., 2020)
- **Chelators** turn metallic ions into water-soluble compounds, making them transportable in the soil and within the plant. There are phytochelatins naturally present, but synthetic phytochelatins such as EDTA can further improve uptake.
- Plant-growth-promoting **bacteria** can sometimes decrease metal uptake but often increases it along with plant growth.
- Conventional breeding and genetic engineering can produce strands that are tolerant to otherwise toxic levels or metal or show increased metal accumulation.

# Dubchak & Bondar (2019) on **radionuclides**

- Only **Cs**, **U** and **Sr** showed satisfying results
- “phytoremediation of $^{137}Cs$ contaminated plot will return land to general use 30 years earlier than without any action”
- Additives: “shoots U concentration in plants grown in a U-contaminated soil increased to more than 5000 mg kg$^{-1}$ in **citric acid** treated soil compared to 5 mg kg$^{-1}$ in control pots”
- Rhizofiltration: “the three-pond system with a flow rate of 1000 l day$^{-1}$, removed 99.3% of the radioactivity” for U, and 98% for Sr

*Above: Cesium*
*Below: Strontium*
*[Wikimedia Commons]*

# Merkl et al. (2005) on **petroleum**

- Heavier hydrocarbons sink into the soil and break its structure.
- Phytoremediation is possible, based on three observations
  - “Plants can enhance microbial degradation by providing **oxygen** in the root area”
  - “Molecular oxygen is required for substrate **oxidation**”
  - “**microorganisms** are stimulated by root exudates”
- Tested the ability of several species of legumes and grass to “stimulate microbial degradation in soil contaminated with 5% (w/w) of a heavy crude oil”
- Soil planted with *Brachiaria brizantha* and *Cyperus aggregatus* “showed a significantly lower oil concentration”, and “a positive correlation between root biomass production and oil degradation was found.”

# Yang et al. (2020) on microbes with heavy metals

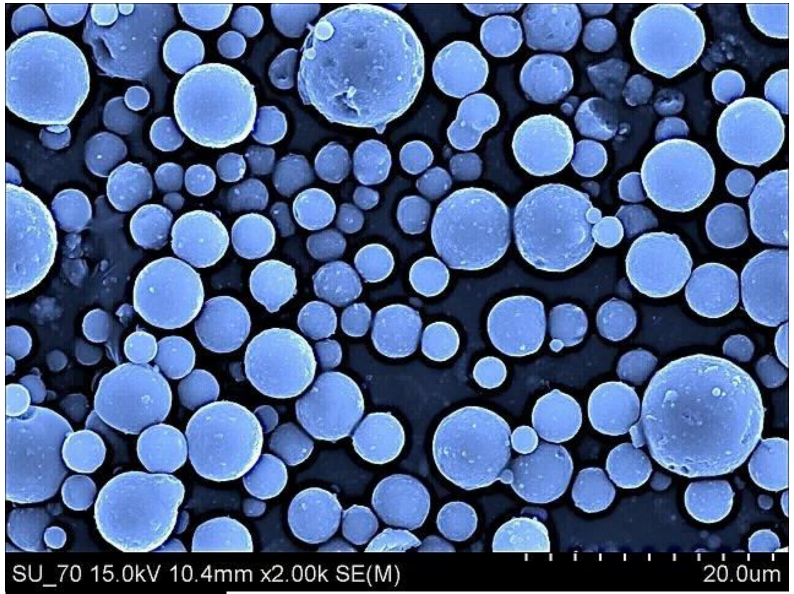
- "Bacillus, Escherichia and Mycobacterium" live in the rhizosphere.
- Three chemical processes:
- **Absorption**: cations bind to negatively charged microbial cells
- **Oxidation-reduction** (redox): enzymatic processes reduce ions to less toxic species, eg. Pb(II) to Pb(I)
- **Precipitation**: amino acid and organic acids dissolve metallic compounds, eg. oxides

### Other processes

"Other beneficial compounds produced by rhizobacteria include enzymes, osmolytes, biosurfactants, siderophores, nitric oxide, organic acids, and antibiotics. These may be responsible for suppression of pathogenic and deleterious organisms, improved mineral uptake, associative nitrogen fixation, tolerance to abiotic stresses, or production of phytohormones."
(Yadav et al., 2018)

# Song et al. (2019) on nano-scale additives

- Nano-materials bond with pollutants and facilitate uptake or immobilization.
- For lead, the extraction rates using ryegrass (*Lolium perenne*) ranged from 17% to 32% without, and from 30% to 44% with the addition of **nano-hydroxyapatite**.
- For Cadmium, the addition of 1g/kg of **nano zero-valent iron** (nZVI) to support the soybean plants increased accumulation in the roots by as much as 73%.
- The uptake of trichloroethylene was increased by 82% with the addition of 15mg/L of **fullerene**.
- **Carbon nanotubes** can adsorb pollutants directly.
- nZVI can directly induce a dechlorinating reaction and also adsorb ions.



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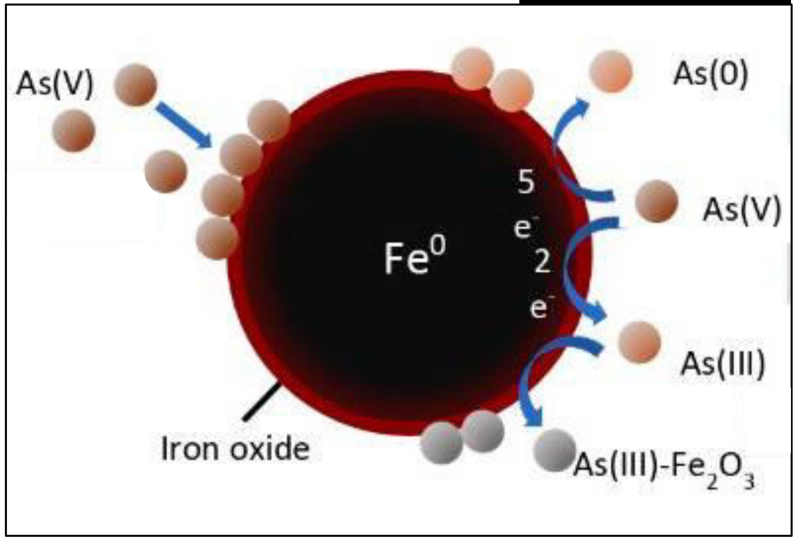


# Wiszniewska et al. (2016) on organic amendments

- Agricultural waste, “biochar, humic substances, plant extracts and exudates”
- Additives may increase pollutant uptake but also disrupt certain equilibriums. For instance, by increasing the immediate availability of **all** metals, synthetic chelators drive the depletion of useful metallic ions in the soil, hindering plant growth in the long run.
- Mostly centered on **decreasing the bioavailability** of metals by increasing the quantity of soluble organic matter
  - decrease of heavy metals As, Cd, Cu, Pb, Zn in the shoot, increased Cd **immobilization**
  - “organic amendments are considered especially effective in Cr stabilization”

# Wiszniewska et al. (2016) on organic amendments

- But **certain amendments** can also **improve** or even enable extraction
  - "the addition of **peat** reduces the time needed for removal of 50% of soil B content", perhaps because "the complexation of trace metals by humic and fulvic acid significantly affects their bioavailability", "addition of organic matter stimulated B translocation to upper parts of the plants"
  - "**molasses** have been found to increase densities of soil bacteria responsible for degradation of royal demolition explosive (RDX). Interestingly, phytoremediation without addition of molasses did not enhance RDX degradation"
- All parameters must be monitored at the same time: "Simultaneously, limited phytoextraction of toxic elements (Cr, Cd, Ni and Pb) occurs, most likely due to pH increase"
- Biochar addition increased fungal community response in an alfalfa sanitation experiment. (Zhang M. et al., 2018)

# Phytoremediation in water (Lone et al., 2008)

- The main pollutants are nitrate and phosphorus (eutrophication), sulphate, ammonia, coliform, dyes, plastic…
- **Rhizofiltration** is the main mechanism and happens in the **same way as for soil**.
- The roots of Indian mustard (*Brassica juncea*) working well on Cd, Cr, Cu, Ni, Pb and Zn, and the roots of sunflowers on Pb, U, Cs and Sr…
- Duck weed (*Lemna minor*) was found to be a good accumulator of Cd, Se and Cu; sharp dock (*Polygonum amphibium*) of N and P, water dropwort (*Oenathe javanica*) of Hg, calamus (*Lepironia articulata*) of Pb, brake fern (*Pteris vitta*) for As…

# Wei et al. (2021) on phytoremediation in air

- plants “absorb atmospheric particulates by leaf adsorption”
- “plants absorb **volatile organic compounds** (VOCs) through stomata during normal gas exchange and convert them into amino acids”
- Most studied compounds: formaldehyde, benzene, toluene
- **Fine particulate matter** (PM2.5) is deposited on the leaves or absorbed through the stomata.
- Leaf area, roughness (eg. hairy leaves) and stomata size are the parameters.
- Certain species can absorb specific pollutants, eg. NO2 plays a role in *Magnolia*’s metabolism.

# Q2. When to intervene ?

# Thresholds in soils in Switzerland

- There are three thresholds: indicative, investigation, intervention. Each allows the government certain measures.
- Compared to other countries, intervention thresholds are much higher, eg. 50 mg/kg soil for Hg versus 2 mg/kg in Germany or Finland.
- Under this threshold, only preventive, less drastic measures can be taken.
- Over this threshold, the measures are more drastic than in other countries.

| Thr. | Canton responsibility |
|---|---|
| Indicative | *Origin ?*<br><br>> Measures to prevent further increases. |
| Investigation | *Risk to people, animals and plants ?*<br><br>> Preventive measures. |
| Intervention | > Corrective measures. |

# Thresholds established by RS 814.12

| **Threshold** | Indicative | Investigation | | | Intervention | | |
|---|---|---|---|---|---|---|---|
| ***Use*** | | *Food crops* | *Fodder crops* | *Ingestion risk* | *Agri- and horticulture* | *Gardens* | *Playing fields* |
| **Depth (cm)** | | 0-20 | 0-20 | 0-5 | 0-20 | 0-20 | 0-5 |
| Chrome (Cr) | 50 | | | | | | |
| Nickel (Ni) | 50 | | | | | | |
| Copper (Cu) | 40 | | 150 | | 1000 | 1000 | |
| Zinc (Zn) | 150 | | | | 2000 | 2000 | |
| Molybdenum (Mo) | 5 | | | | | | |
| Cadmium (Cd) | 0.8 | 2 | 2 | 10 | 30 | 20 | 20 |
| Mercury (Hg) | 0.5 | | | | | | |
| Lead (Pb) | 50 | 200 | 200 | 300 | 2000 | 1000 | 1000 |
| Fluor (F) | 700 | | | | | | |

Values are in mg/kg dry matter until 15 % organic matter and mg/dm3 above.

# Other limits

Limits for heavy metals in P-based fertilizers (Mayer et al., 2019)

- The intervention thresholds for agricultural soils are very high.
- To prevent the problem rather than fix it, limits are set for fertilizers.
- The limits are expressed in phosphorus equivalent.
- Pesticides 0.01 mg/kg soil (Switzerland)

Lower threshold

- If the plant is appropriate, pollutant extraction will occur.
- However, for metals, there may not be **enough essential metals** to support optimal plant growth. This is aggravated by chelators.

| | mg/34kg P per year |
|---|---|
| Cd | 39 |
| Ni | 890 |
| Cr | 420 |
| Hg | 12 |
| As | 140 |
| Pb | -53 |
| Zn | 14000 |
| Cu | 1720 |

# Thresholds in water (Babu et al., 2021)

Higher threshold

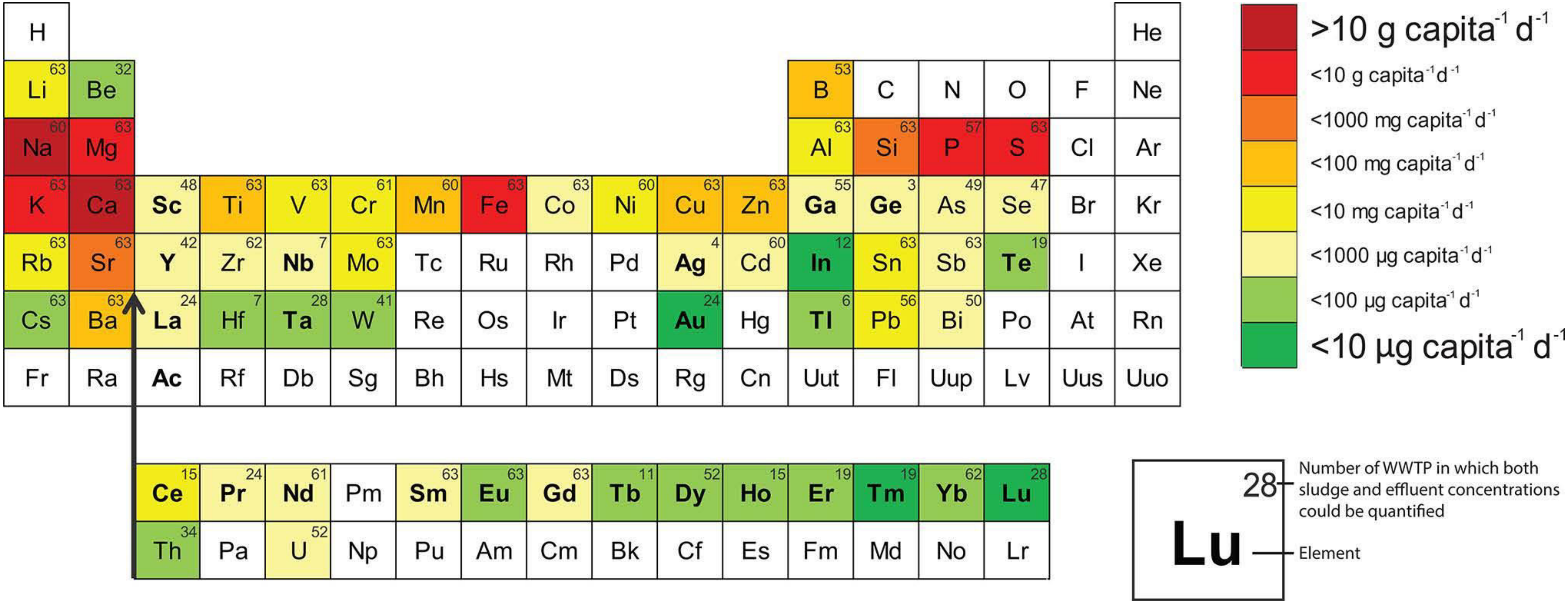
- As, Cd, Zn 5 µg/L water (Australia, South Africa)
- Pb 10 µg/L water (WHO)
- Cu 50 µg/L water (WHO)
- Cr, Ni 100 µg/L water (South Africa)
- Pesticides 0.1 µg/L water (Switzerland)
- Medicine,  0.1 µg/L water (Switzerland)

Lower threshold

# Improvement targets in Switzerland

- Every year, Swiss treatment plants let **3000 kg Ar**, **43 kg Au**, 1070 kg Gd, 1500 kg Nd and 150 kg Yb escape. This amount of silver and gold alone is worth about 3 million CHF. (tdg.ch)
- More complex micropollutants are studied but do not have appropriate phytoremediation strategies yet. The list of candidate substances has 250 items, including 127 phytocontrol products. Note that EDTA, a **chelator**, is on this list, though considered “easily biodegradable”. (Götz et al., 2011)

# Per-capita output of elements (Vriens et al., 2017)




Data collected from 64 treatment plants in Switzerland in February and March 2016

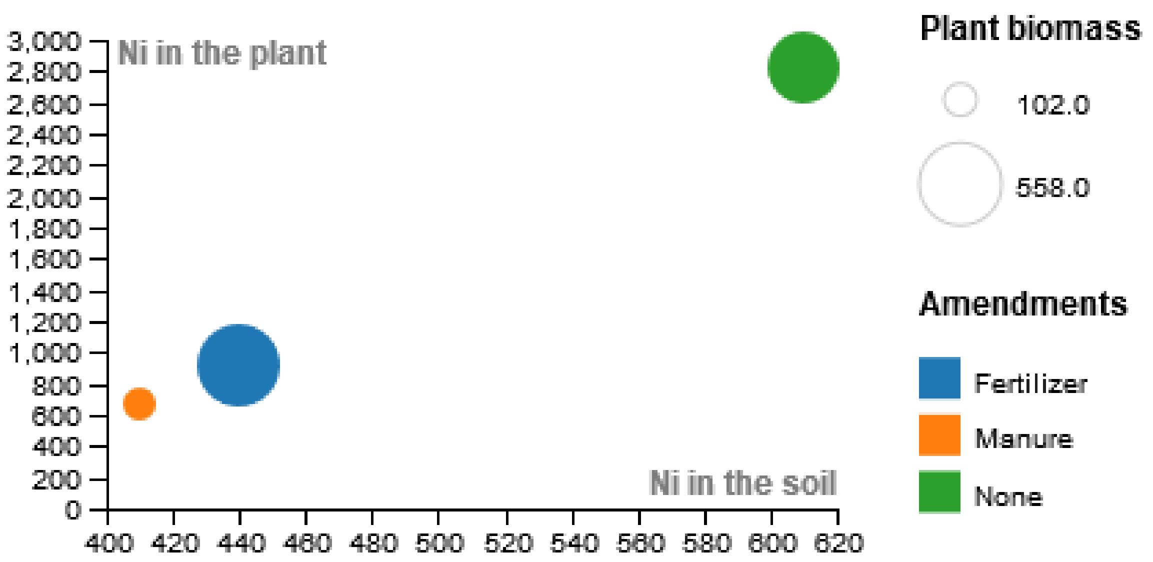
# Q3. Is there a universal method ?

# Phytoextraction in Albania (Osmani et al., 2015)

- Site of an old metallurgical complex in Elbasan, now used as residentia and for agriculture.


- Chosen species *Alyssum murale* (nickel hyperaccumulator)

| | | Plot I | Plot II | Plot III |
|---|---|---|---|---|
| | *Amendments* | *None* | *Fertilizer* | *Manure* |
| Before | Ni in the soil [mg/kg soil] | 610 | 440 | 410 |
| After | Plant biomass [g] | 429 | 558 | 102 |
| | Ni in the plant [mg/kg biomass] | 2818 | 920 | 677 |

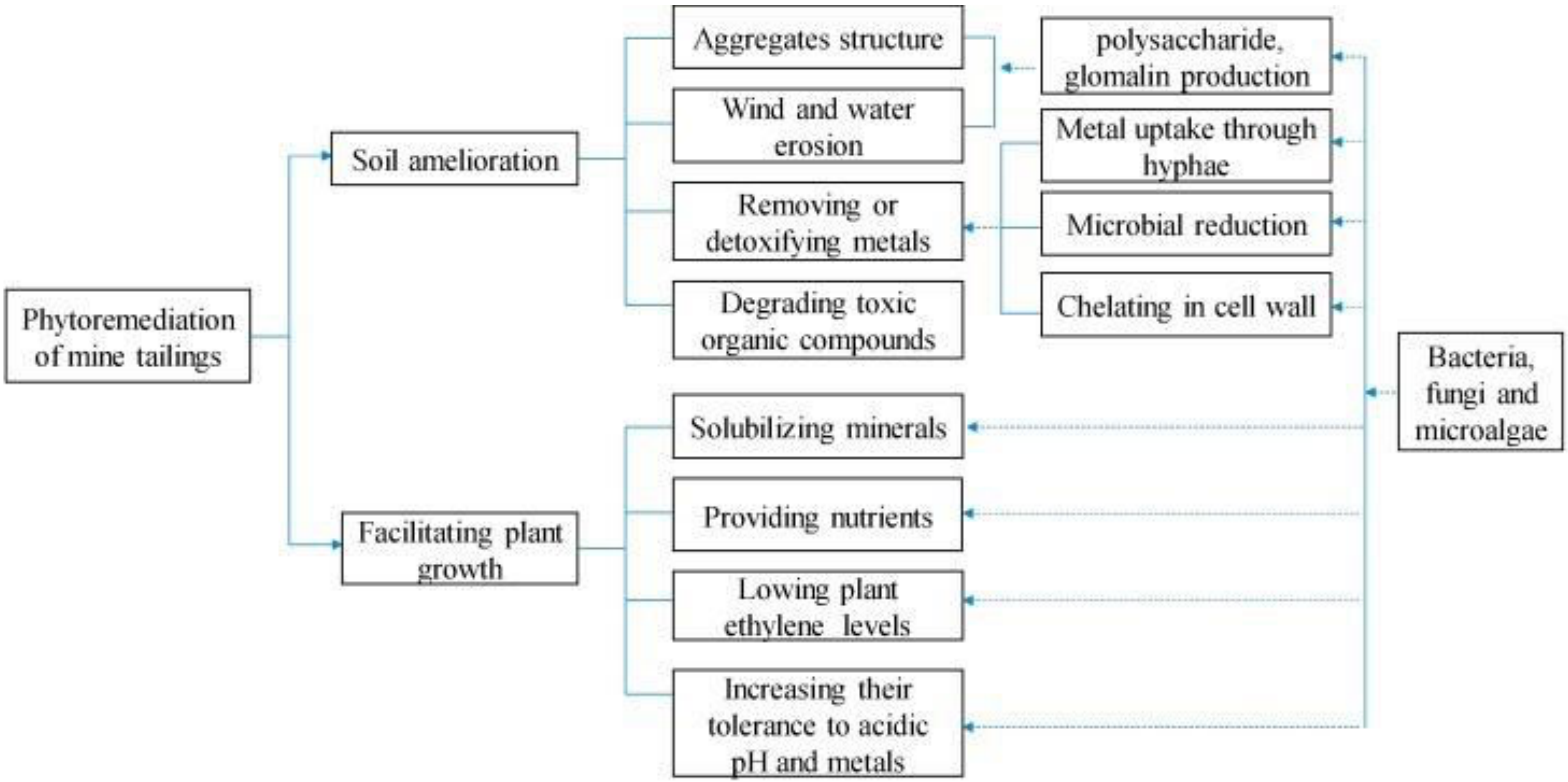



- The WHO limit for Ni in plants is 10 mg/kg !

# Developing a strategy

- Rely on past experiments: literature reviews are always **filled with tables** of species names, appropriate conditions, targetable pollutants and sometimes even observed removal rates.
- It’s easy to take a pick and try it on a new site
  - *Zea mays* showed 97% decrease of Atrazine (pesticide) in soil. (Wei et al., 2021)
  - *Ceratophyllum demersum* accumulated 13% to 84% of Cr and 92% to 95% of Pb in wastewater. (Yadav et al., 2018)
  - *Eichhornia crassipes* accumulated 98% of Cd, 99% of Cu, 84% of Zn and 98% of Pb in an hydroponic system. (Yadav et al., 2018)
  - Species of *Helianthus* reduced Uranium concentration in water from 21–874 ug/l to <20 ug/l (Padmavathiamma & Li, 2007)
- For each site, a different strategy can be devised.
- Pollutant mix, soil conditions and desired state are the three main parameters.

# A strategy for mine tailings (Wang et al., 2017)

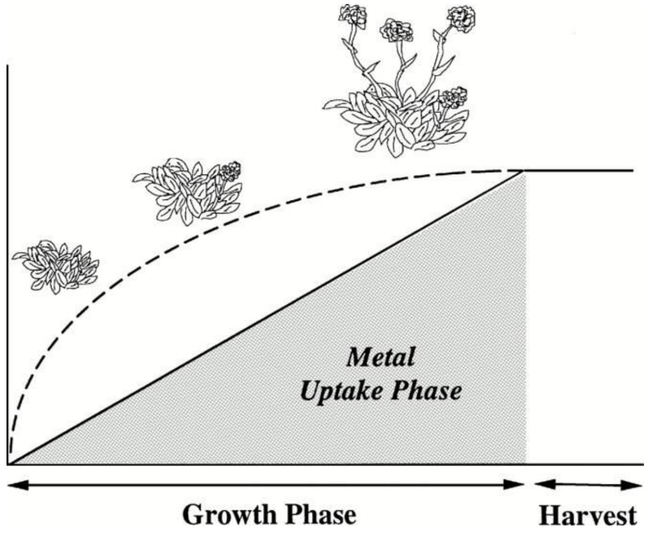


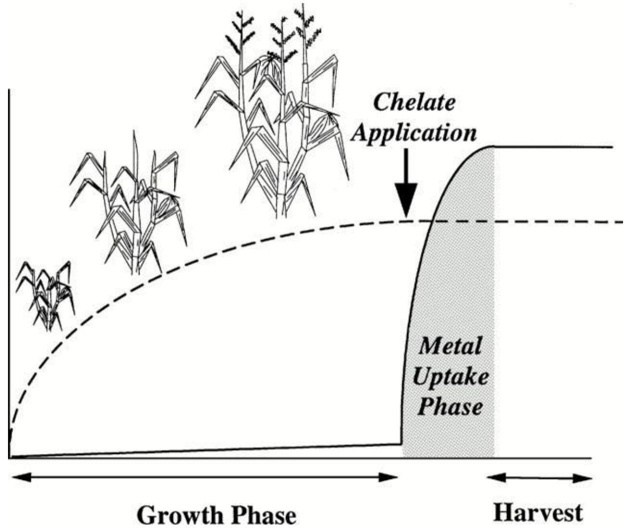

Contribution of microorganisms to the phytoremediation of mine tailings.

# Foregoing hyperaccumulators

- Many hyperaccumulators have insufficient biomass.
- One solution can be to use a species with **normal uptake** but high biomass, and make the metals more bioavailable **with chelators**. (Salt, Smith & Raskin, 1998)

- Trees are also poor accumulators of metals but have the highest **biomass**, and deep, massive **root systems**.
- Phytostabilisation can be achieved by **physical** as well as **chemical effects**. Roots and litter decrease leaching. Dangerous compounds can be reduced (eg. Cr(IV) to Cr(III)) or mineralized (eg. lead to chloropyromorphite as observed with grasses). (Pulford & Watson, 2003)




Continuous and chelate-assisted phytoremediation. Dashed line: shoot biomass. Solid line: metal concentration in the shoot.
(Salt, Smith & Raskin, 1998)

# Challenges in application

- The cost is low but not null. The efficacy in the field must be known before a phytoremediation system can be built.
- Once built, its efficiency must be **monitored**. Soil chemistry analysis can be expensive.
- With increased metal quantities in the stems and leaves, is plant-consuming **wildlife** safe from intoxication ?

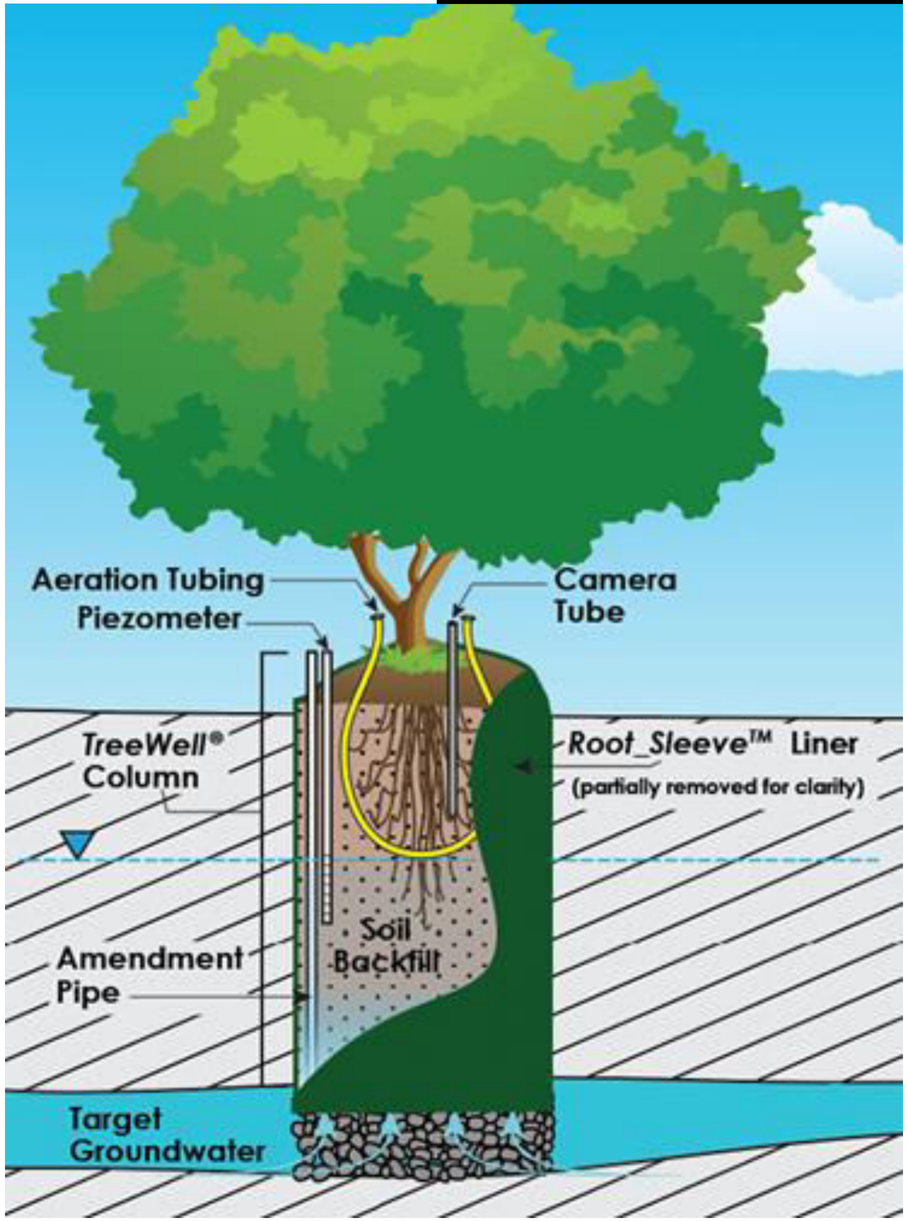
[Stantec]

# Wrapping up

# Conclusion

- Given the complexity of chemical and biochemical interactions, research remains empirical and very much applied.
- Phytosanitation technologies are commercially successful because they allow exceeding **regulatory requirements** at unbeatable **cost**. Phytoremediation systems that permit the same will also encounter commercial success, unlocking funds for further development.
- Phytoremediation is appropriate for diffuse and relatively shallow pollution. That's a limit but also an opportunity.

TreeWell technology [Geosyntec]



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- Plant hormones