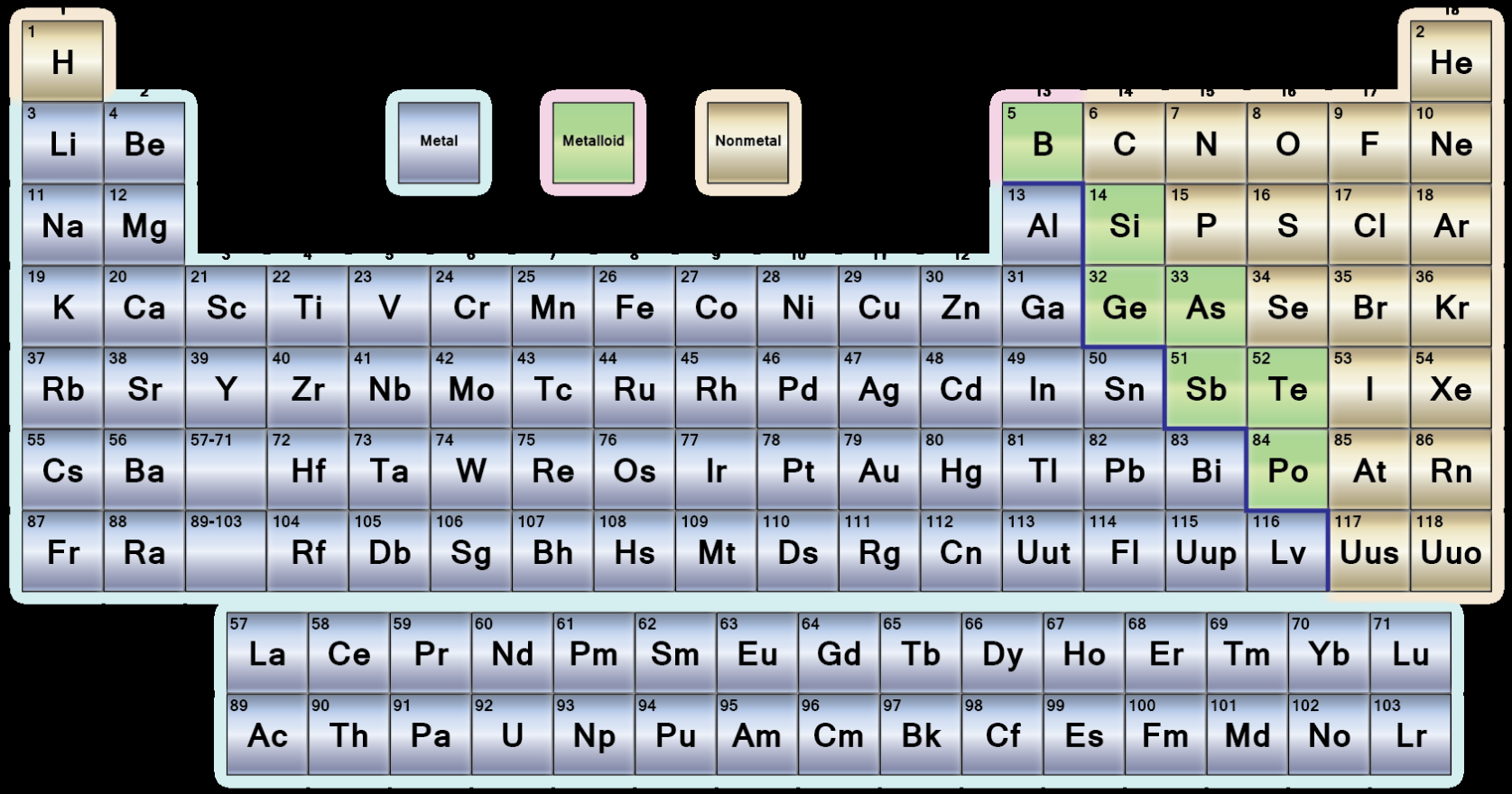
Trace elements/metals in the agriculture environment

What are trace elements (TE)?

- Elements present in natural material at concentrations of <1000 mg kg^{-1}
- Most elements of the periodic table are trace elements
- Some TEs are essential to life but many can be toxic at high concentrations
- Trace elements that might be of environmental concern are: As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Cs, Sn, U, Be, and Tl.

Typical metals, non-metals, metalloids



Metal

- usually solid at room temperature (mercury is an exception)
- high luster (shiny)
- metallic appearance
- good conductors of heat and electricity
- malleable (can be bent and pounded into thin sheets)
- ductile (can be drawn into wire)
- corrode or oxidize in air and sea water
- usually dense
- may have very high melting point
- readily lose electrons

Non-metal

- dull appearance
- usually brittle
- poor conductors of heat and electricity
- usually less dense, compared to metals
- usually low melting point of solids, compared with metals
- tend to gain electrons in chemical reactions

Metalloid

- dull or shiny
- usually conduct heat and electricity, though not as well as metals
- often make good semiconductors
- often exist in several forms
- often malleable
- may gain or lose electrons in reactions

Sources of TE originate from natural and anthropogenic sources

ENERGY and MINERAL CONSUMPTION are the main contributors to TE pollution in water

And MILITARY ACTIVITIES:

And INDUSTRY AND URBANIZATION:

And AGRICULTURE:

And natural-occurring minerals from weathering of soil in California

And natural Karst carbonate depositions of Se in Guizhou, China

Additional sources of TE contamination

- Metal mine tailings
- Disposal of high metal wastes in improperly protected landfills
- Leaded gasoline and leaded-based paint
- Land application of fertilizers, animal manure, biosolids, compost, pesticides, coal combustion residues
- Atmospheric deposition

Mining operations creates mine wastes

In agricultural soils naturally high in Tes, excessive irrigation has an effect on TE movement and their availability for plant uptake

Irrigation affects solubility and hence bioavailability. Importantly, excessive irrigation also affects runoff and groundwater contamination.

Extreme example, drainage ponds in the westside of the SJV

TEs threats to animal/human health

Acid mine seepage in South Dakota

Contaminated soils and water

ENTRY Into FOOD CHAIN

DIRECT INGESTION OF SOIL

INHALATION OF WIND-BLOWN TE DUST

TEs health hazard to humans

- Cancer causing (As, Be, Cr, Ni, and perhaps Cd)
- Chronic lung disease (Be and Cd)
- Neurological and reproductive disorders (Pb and Hg)
- Kidney disorders (Pb and Cd)

Zinc and Cd in the environment

- The most important source of Zn and Cd contamination in soil is from mine waste and smelter emission
- Zinc is both deficient and phytotoxic element in soils, the latter due to industrial contamination
- Zn and Cd uptake and transport to shoot are competitive with each other

Soil contamination of Cd

- Sources of Cd are extensive: use of Cd-rich phosphate fertilizers (e.g., Salinas Valley), high Cd biosolids, or its natural origin from mineralization of high Cd:Zn ratio marine shale parent rocks (Salinas, CA).

Cd uptake in rice

- Extensive areas of paddy rice soils in Japan, China, and Thailand have become contaminated by Cd mine and smelter emissions.
- Rice readily accumulates Cd in excess of limits (0.4 mg kg^{-1} fresh weight for brown rice) when soils contain as low as 1.5 mg kg^{-1} Cd – especially in flooded soils.

Cd in tobacco

- Like rice, tobacco also accumulates Cd very effectively, especially on acidic soils.

Influences on Cd uptake

- Low soil pH promotes Cd uptake by plants
- Soluble chloride in the soil increases Cd phytoavailability (Swiss chard and wheat)
- Zn competes with Cd for uptake by most plants

Arsenic

- Contaminated water used for drinking, food preparation and irrigation of food crops pose the greatest threat to public health from arsenic.
- Arsenic is highly toxic in its inorganic form.
- Arsenate is taking up similarly as phosphate

The greatest threat to public health from arsenic originates from contaminated groundwater. Inorganic arsenic is naturally present at high levels in the groundwater of a number of countries, including Argentina, Bangladesh, Chile, China, India, Mexico, and parts of the USA (California).

Sources of As

- Aerosol deposition from mine waste
- Contaminated groundwater
- Military activities (especially during WWI)
- Wood preservatives

Lead (Pb) in the environment

- For hundreds of years, lead had been mined, smelted, refined, and used in products (e.g., as an additive in paint, gasoline, leaded pipes, solder, crystal, and ceramics)
- Mining, smelting, and refining activities have resulted in substantial increases in lead levels in the environment

Possible ways to increase Pb intake in humans:

- ingestion of lead-contaminated water, soil, paint chips, or dust;
- inhalation of lead-containing particles of soil or dust in air; and
- ingestion of foods that contain lead from soil or water.

Pb food chain transfer

- Direct soil ingestion is the main route of human and wildlife contamination.
- If plants are grown in soils with P deficiency or no P fertilizers were added, plants can accumulate and translocate high amounts of Pb
- P causes the formation of an insoluble Pb-phopshate compound in roots.
- Thus, normal soil and plant Pb chemistry prevents plant Pb uptake/translocation to any meaningful extent

Criteria to estimate TEs threats are:

- Bioaccumulation
- Toxicity
- Persistence

BIOAVAILABILITY OF **TRACE ELEMENTS**

It measures the amount of metals that are labile (loose/available) for root uptake

It depends on:

- Pollutant's chemical properties
- **Soil properties**
- Biological activity (microorganisms)

SOIL pH

SOIL REDOX CONDITIONS

PRESENCE OF HIGH QUANTITIES OF ORGANIC MATTER

There is no single standard technique for the assessment of either plant availability of contaminants or their ecotoxicological impacts of soil biota.

The soil-plant barrier

- Can limit transmission of many metals through the food chain either by:

  1) soil chemical processes that limit solubility (i.e. soil barrier) and uptake by the plant,

  2) plant senescence from phytotoxicity (i.e. plant barrier) before they reach levels in the edible parts of plants.

Entry of TE into the plant

- Predominately through roots
- Lesser extent through leaves (stomata, aqueous pores)

Se
Se
Se
Se
Se
Se
Se
Se
Se
Se
Se
Se
Se
Se
Se
Se
Se
Se
Se
S

Mechanism of ion antagonism/synergism entering normal crops

- Selenate vs sulfate
- Phosphate vs arsenate
- Cadmium vs zinc
- Cadmium vs chloride
- Selenium vs mercury

Metal tolerance

- The presence of a plant species on metal-contaminated soil implies that it is tolerant of metal toxicity.
- Such edaphic adaptation necessitates a specialized physiology
- The strategies of survival are tolerance and avoidance of metal toxicity
- Two main plant strategies are suggested: accumulators and excluders

Metal homeostasis

- Once the metal enters the root cells it needs to be chelated to be transported through the membranes and into the aerial parts of the plant
- Metals can be hydrated or chelated (bound to ligands) to reduce toxicity
- Free metals in the cytoplasm are toxic to the plant

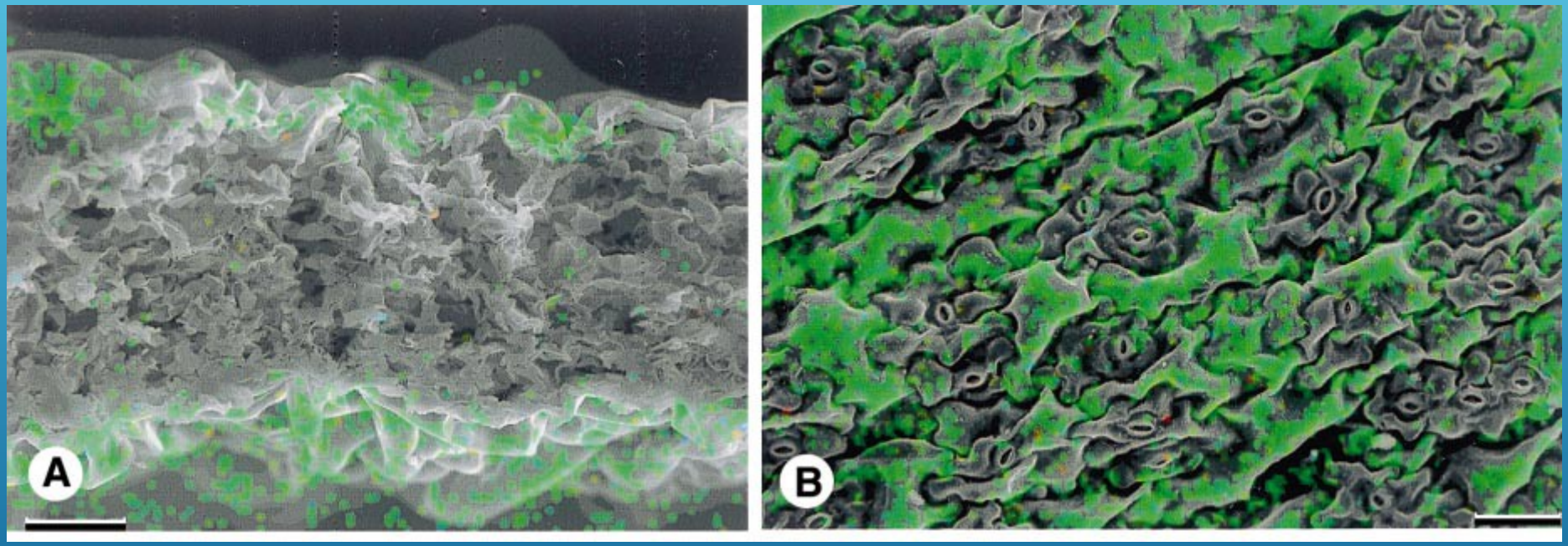
Internal detoxification

- How and where are these high amounts of metals stored in the plant to avoid toxicity and plant senescence?
- What are the mechanisms of internal detoxification?

Mechanisms of metal tolerance

- Largely internal = active detoxification of metal ions
- The sites of detoxification differ between excluders (ROOT) and accumulators (SHOOT)

It appears that most metals (Ni, Cu, Zn) are accumulated in the vacuoles of leaf epidermal cells



Green coloration in the X--ray maps indicates the presence of nickel. Note the absence of nickel from guard cells. Cross section (A) and surface view (B) of a *Thlaspi pindicum* leaf.

Metal hyperaccumulator plants

- Zn and Mn = 10,000 mg kg^{-1} dry shoots
- Ni, Co, Pb, and As = 1000 mg kg^{-1} dry shoots
- Cd = 100 mg kg^{-1} dry shoots

when grown in their natural environment

<u>Such concentrations are far in excess of those normally considered to be phytotoxic</u>

<u>Only 0.2% of all angiosperm are metal hyperaccumulators</u>

Hyper-accumulators

- The term hyperaccumulator was first observed in *Sebertia acuminata,* which produces a blue-green latex containing nearly 26% nickel in a dry matter basis.

The magic!

- Hyperaccumulators are able to take up 100 times more metals than normal crops
- They take up huge quantities of metals even if the concentration in the soil solution is very low
- It seems that hyperaccumulators do not possess special mechanisms for attacking the non-labile pool of metals but they instead access the same labile pool of metals as normal crops do

Evolutionary advantage of hyperaccumulators

- Hyperaccumulating metals is metabolically costly for the plant, and metals can cause stress that generates reactive oxygen species (ROS) that can damage cellular processes
- <u>What are the benefits?</u>

Hyperaccumulation may be a developed defense against herbivores, pathogens, soil bacteria

Examples of accumulator species

- *Thlaspi alpestre (p.cress*

- *Minuartia verna (sandwort)*

- *Armeria maritima (sea pink)*

Zn and Cd hyperaccumulators

- *Thlaspi caerulescens (pennycress)* is the most known Zn hyperaccumulator (1%)
- An ecotype from Southern France can take up high amounts of Cd as well

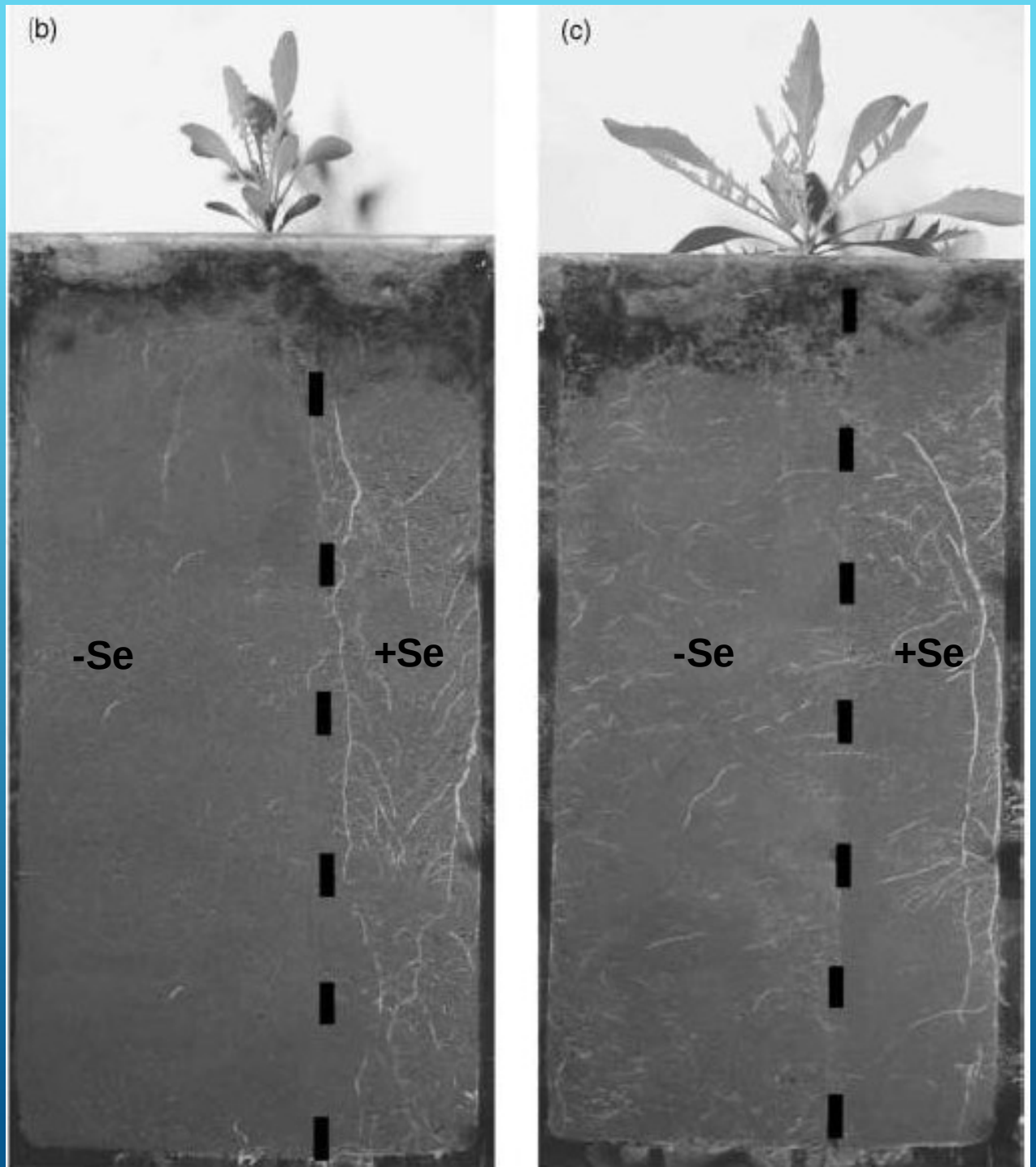
Western Native
Se Hyperaccumulator
Plants

Indicator Species
Require Se in soil to grow and thrive

Astragalus bisulcatus
1.5% Se DWT Fabaceae
15,000 μg Se g^{-1} DWT
two grooved stinky milk vetch

Perennial Plants

Stanleya pinnata
0.6% Se DWT Brassicacea
6,000 μg Se g^{-1} DWT
prince's plume



S. pinnata

Directed Root Growth

Selenate chemotactic root

Se is not essential for higher plants

Pb hyperaccumulators

Two Pb accumulators (<1000mg kg-1)

Hemp dogbane,
Apocynum sp.

Ragweed,
Ambrosia sp.

Ni hyperaccumulators

- At least 300 Ni-hyperaccumulating taxa are known

In EU, Eastern Mediterranean, and Asia Minor

- The genus *Alyssum* and *thlaspi* with the ability to accumulate 0.1-3% Ni

In new Caledonia

Phyllanthus and *Sebertia acuminata*

As Hyperaccumulator

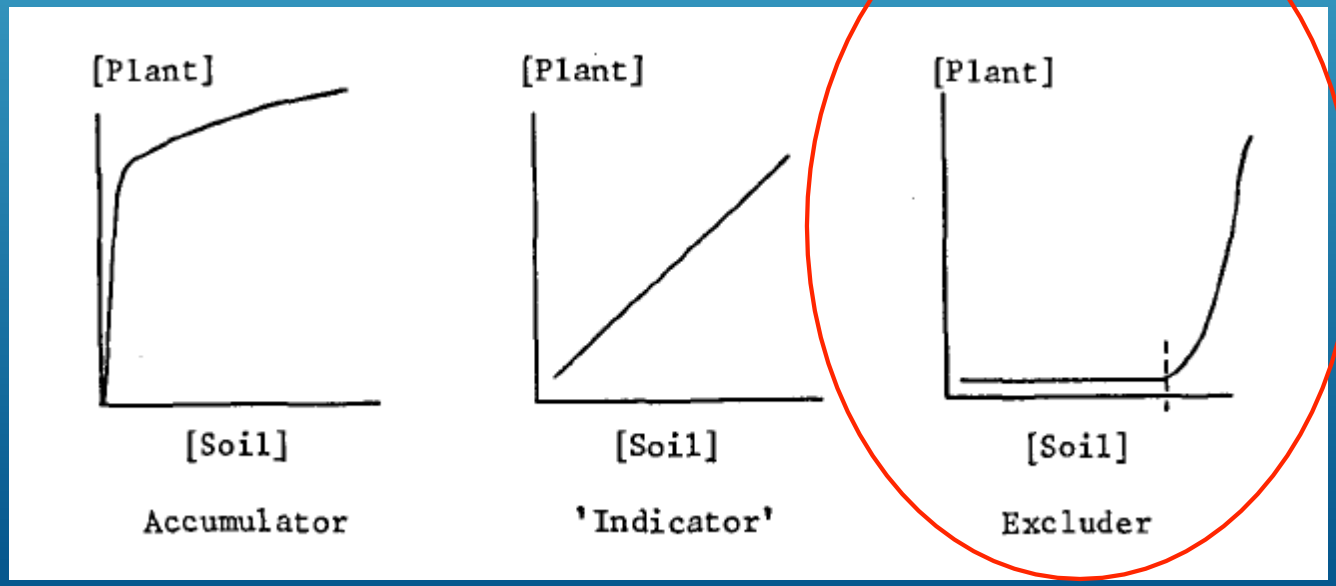
As Hyperaccumulator-Fern (*Pteris vittata*)

- Difficult and time consuming to establish
- Intolerant to cold climate

As enters the root on the high affinity P transporter. Soluble P generally inhibits As uptake, but not in *P. vittata*

Excluders

- Where metal concentrations in the shoot are maintained at a low or constant concentration over a wide range of soil TE concentrations. Above a critical concentration the excluding mechanism breaks down and unrestricted uptake occurs.



Examples of excluder species

- *Silene Vulgaris (bladder)*

- *Lotus corniculatus (birdsfoot trefoil)*

- *Viola calaminaria (pansy)*

Uses of hyperaccumulators

- Remediation of polluted soils
  - Phytoextraction
  - Clean up and produces biomass
  - Clean up and produces fertilizers or used as food supplement (selenium)
- Phytomining
- Phytostabilization of contaminated areas
- Understand the mechanisms of uptake and determine if these traits can be useful for mitigating Zn-deficient crops

Tobacco

Thlaspi caerulescens from Southern France

- Low biomass production
- Env. Adaptability
- Rosett e type (difficult for harvest)

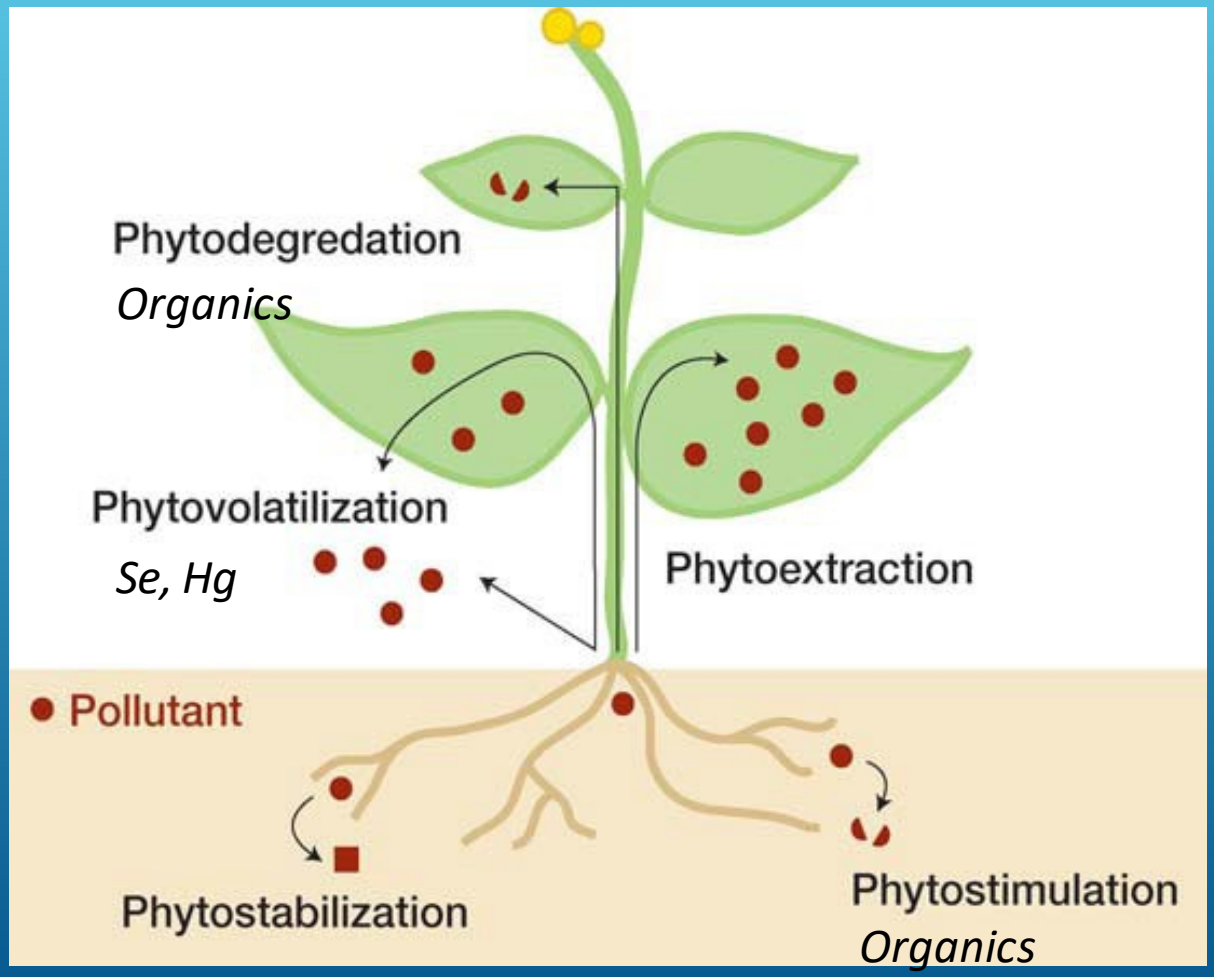
Willow can also be a good Cd accumulator. It is a good source of biomass for biofuel production

Sedum alfredii, low biomass but grows in tropical environments

Biological management of soluble TE at polluted sites

- Plant-based methods (phytoremediation)
- Microbes-based methods (bioremediation)
- Natural attenuation
- Crop selection
- **Objective is to reduce the food chain transfer (soil-plants-humans) of TEs*

Phytoremediation of organic and inorganic pollutants



*Side-note with poplar trees and organic contamination

What is phytoextraction?

- Use of plants to remove TE from the soil plow layer. These TEs are sequestered in the plant's above ground parts that are then harvested through a number of growing cycles

Important factors for the success of phytoextraction

- High biomass production
- High removal of TE by plants (hyperaccumulators)
- Contamination of soil is by one or few TE (hyperaccumulators are specialized for a specific element)
- No time constraints for the remediation of the polluted site (phytoextraction can take decades)
- **Biomass may have commercial value**

When is phytoextraction successful?

- Poplar used for B extraction produces B-rich fodder
- Willow used for Cd removal produces biomass used for gasification
- Broccoli and canola used for Se removal produce Se enriched food and fodder, and residual seed is used as bioherbicide
- *Stanleya pinnata* removes Se and produces Se-enriched plants material for use as Se bio-fertilizer

Example of using Poplar for B removal

- Wood treated with boron chemical in New Zealand caused B leaching into groundwater l
- Hybrids of poplar were grown around and on waste piles. High evapotranspiration rates limit offsite movement of B-rich plume to groundwater
- Poplar accumulated high B levels in the leaves. Poplar wood can be used for energy production and leaves used as B-rich fertilizer/fodder.

Willow and Cd

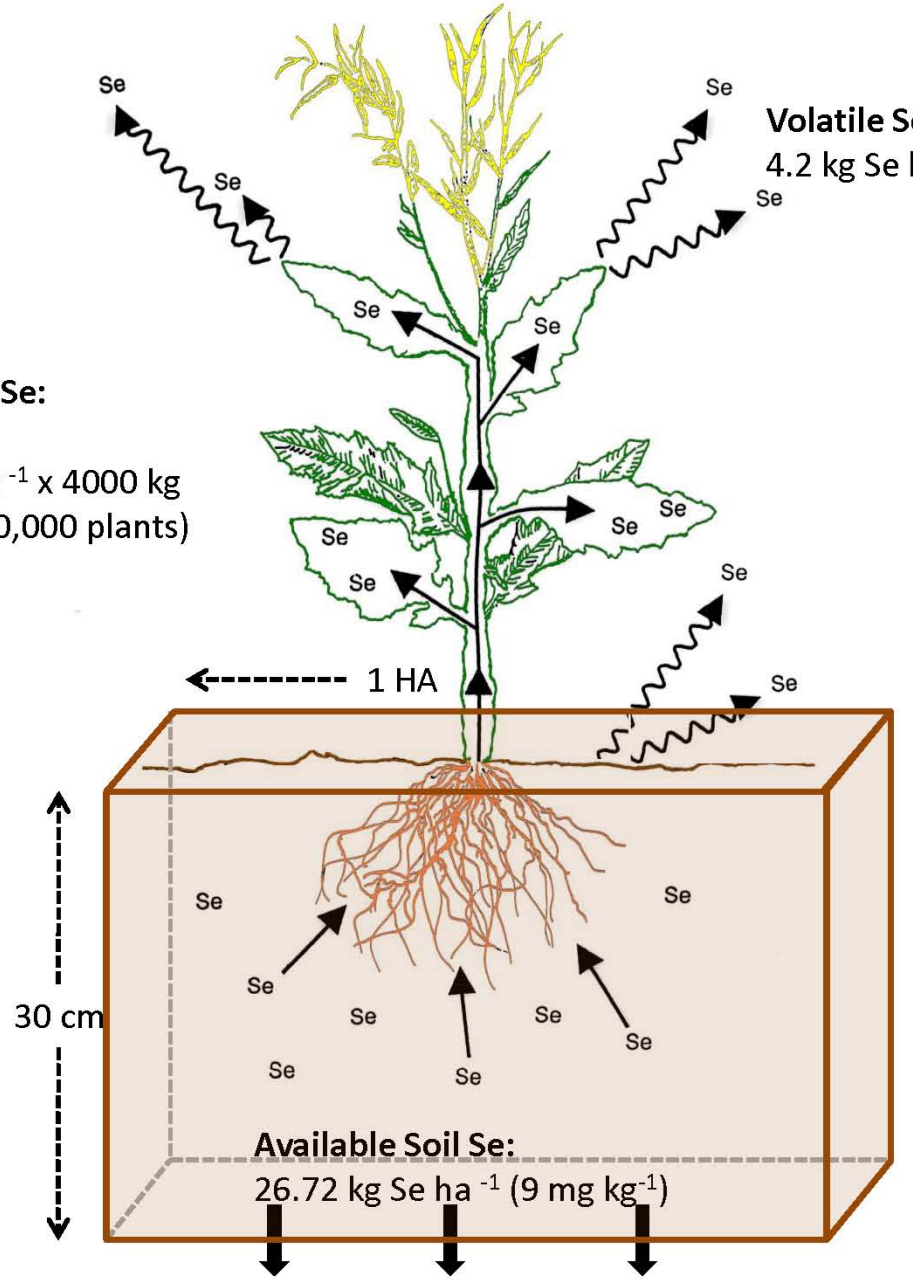
- *Salix* species (poplar and willow) are accumulators of Cd, Zn, and B.
- They can be coppiced every three years with a 15- to 20-year cycle
- Their shoots can be sold as biomass for biofuels or bioelectricity from gasification

1. Grow hyperaccumulators for TE removal

2. Harvest the biomass containing the TE

3. Dispose the metal rich biomass in a lined landfill

True Phytoremediation of Se with Stanleya pinnata



Volatile Se:
4.2 kg Se ha $^{-1}$ (1160 μg Se m^{-2} d^{-1})

Accumulated Se:
2.6 kg Se ha $^{-1}$
(650 mg Se kg $^{-1}$ x 4000 kg DM ha $^{-1}$ for 30,000 plants)

Phytoeffect:
~20% removal efficiency in one year (note: removal efficiency will likely decrease with each subsequent year).

Available Soil Se:
26.72 kg Se ha $^{-1}$ (9 mg kg^{-1})

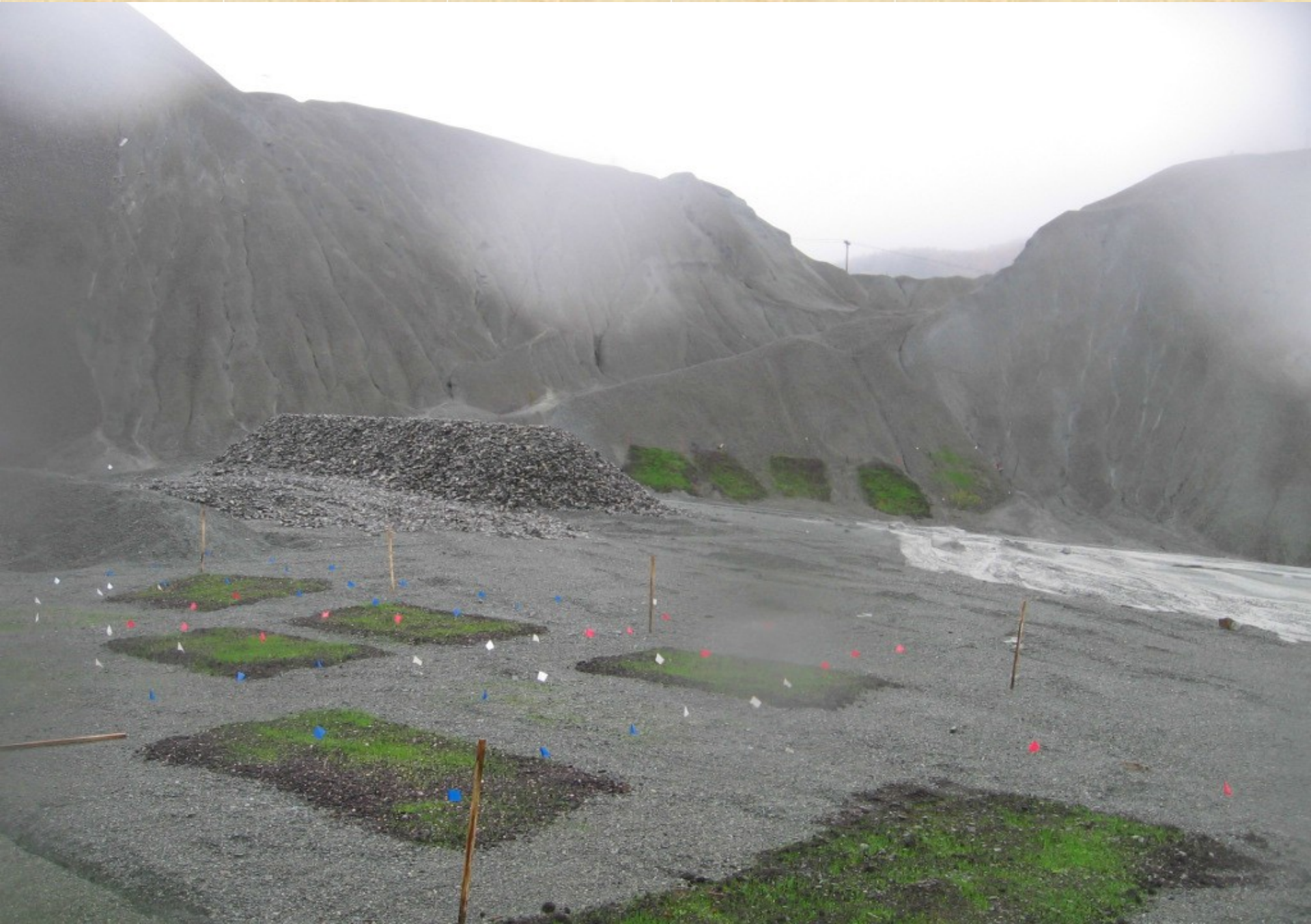
Leaching of Se???

Brassica and Se Removal

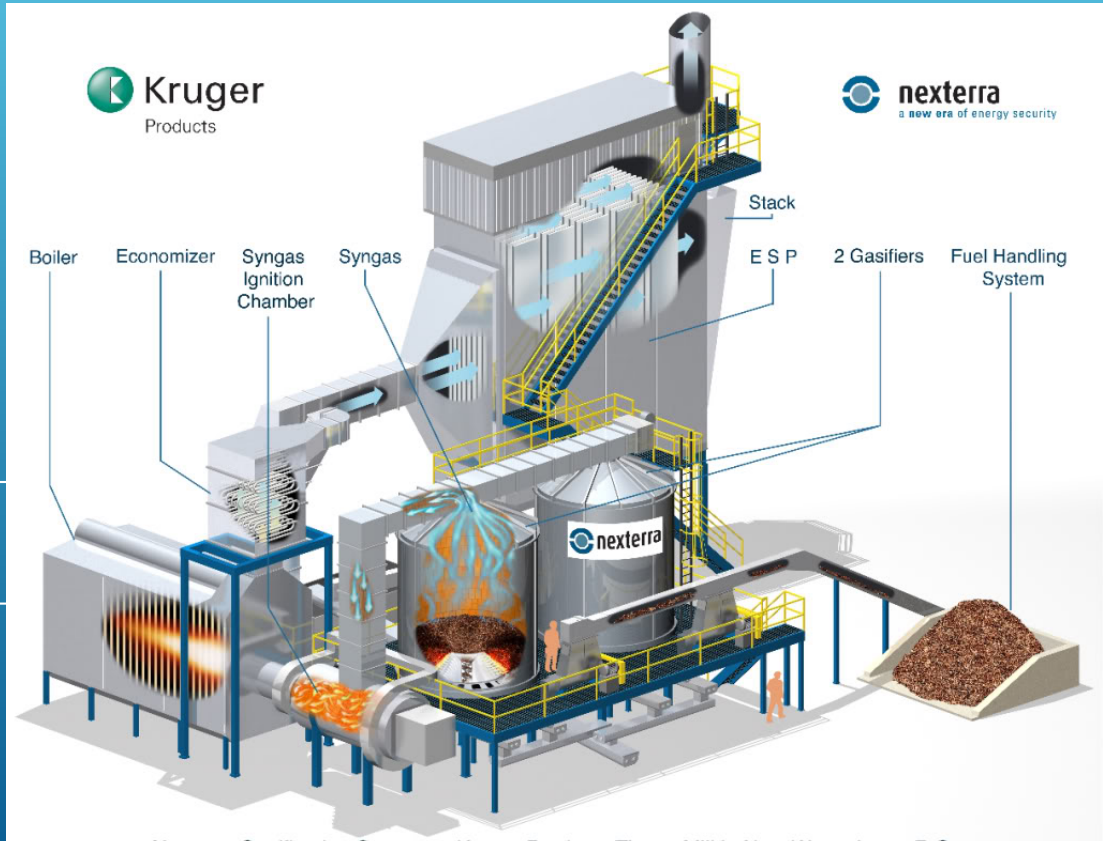
- Canola (*Brassica napus*) can accumulate levels of Se
- Canola oil can be used for biodiesel and residual seed meal as Se-enriched feed
- Canola seed meal can be used as bio-herbicide

Other cropping systems

Cover crops establishment



Trace element laden plant material will be used in gasifier to produce bioelectricity.



Nexterra Gasification System at Kruger Products Tissue Mill in New Westminster B.C.

Biodico Biorefinery Plant

Constructed wetlands for contaminated water

A wetland is a complex assemblage of water, substrate, plants (vascular and algae), litter (primarily fallen plant material), invertebrates (mostly insect larvae and worms) and an array of microorganisms (most importantly bacteria). The mechanisms available to improve water quality include:

- settling of suspended particulate matter
- filtration and chemical precipitation through contact of the water with the substrate and litter
- chemical transformation
- adsorption and ion exchange on the surfaces of plants, substrate, sediment, and litter
- breakdown and transformation of pollutants by microorganisms and plants
- uptake and transformation of nutrients by microorganisms and plants
- predation and natural die-off of pathogens

Use of Vetivier grass

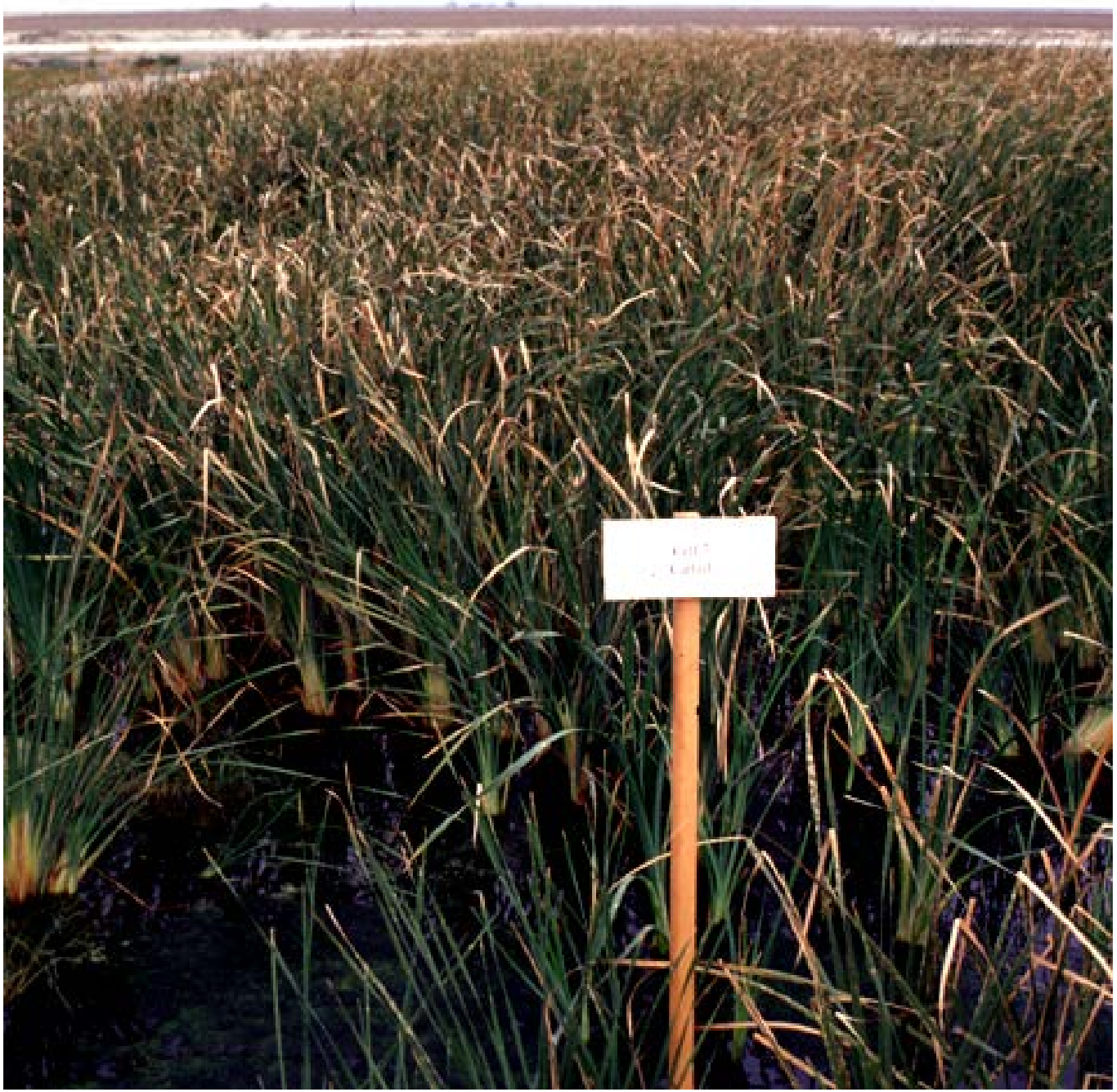
The plant can absorb toxic substances like pollutants, pesticides, and heavy metals into its biomass.
Vetiver is used to purify eutrophicated water in the lake, leachate from garbage landfill, etc.
The plant can also absorb heavy metals from quarry, and such valuable metals can be recycled by extraction from the vetiver biomass.

Pucinellia Distans (salt marsh grass)

It seems to be a B-tolerant species that can be used for phytoextraction of B in wetlands and in soil

Poplar Trees Growing in Selenium-Laden Water

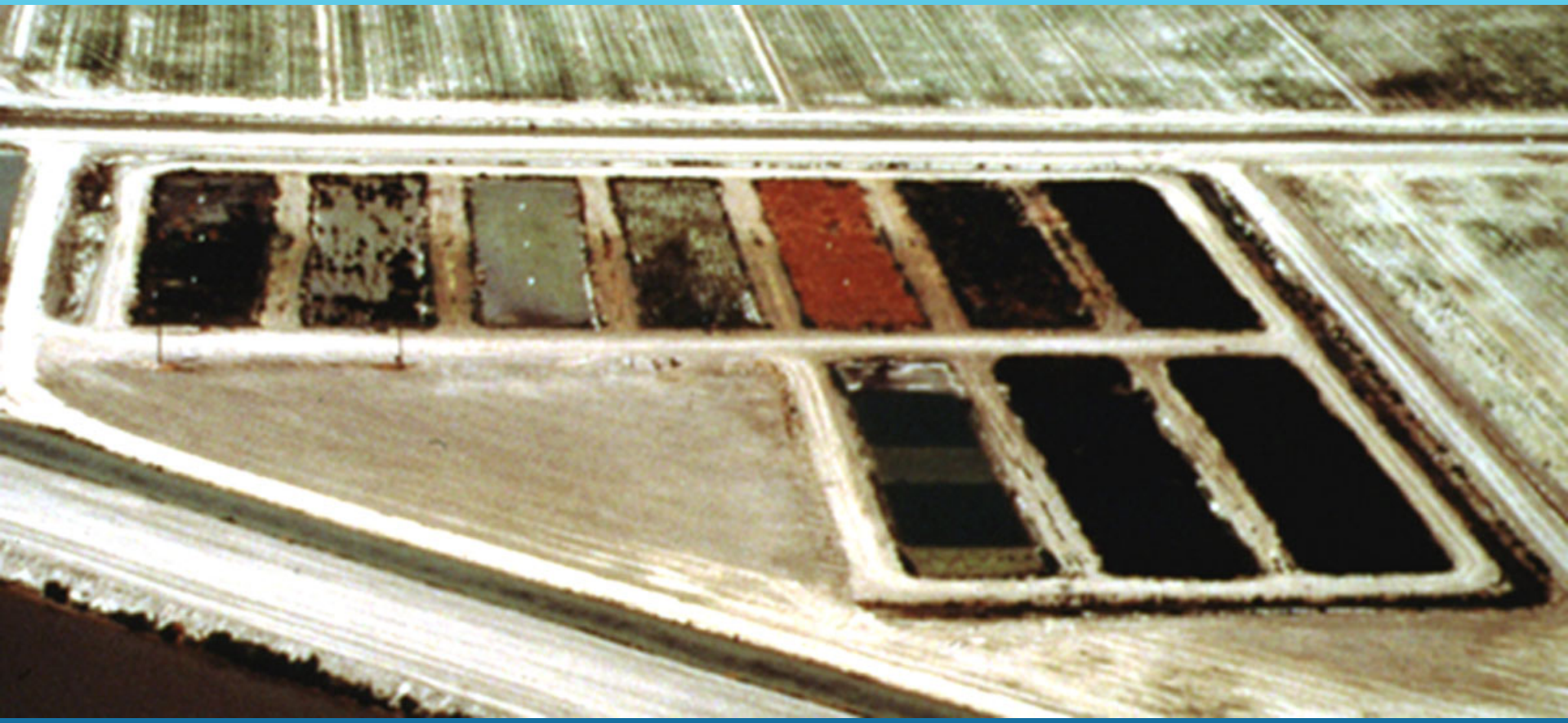
Planting the Wetland Cell



Cattail

(4 months after)

Constructed Wetland for Se Removal



Other species used in wetlands

- Duckweed, brass button, water hyacinth, smartweed, umbrella plant, water zinnia, water lettuce, and mare‘s tail are top plant species accumulating high concentrations of certain toxic trace elements.

Phytomanagement

Recognizing that Tes can be taken up by plants is not all bad. This observation has led to the development of phyto-strategies with wetland or cropping systems with specific plants that can manage content and movement.

Conclusion

The food chain (soils-plants-humans) is the major pathway for human and crop exposure to potentially toxic levels of trace elements. Understanding which pathway the TE uses to enter the plant will help us determine two items: 1) which food crops to grow or which amendments to add to soil to minimize the uptake of TE by the plant and/or 2) can we grow a crop to phytomanage the TE in soil and/or water? Understanding a plant's ability or inability to take up Tes is key to determine if an unwanted TE can eventually be toxic to biological systems.

Phyto-stabilization

- Revegetation of polluted areas that usually barren, thus prone to soil erosion and leaching of TE to groundwater, and represent an ecological hazard to wildlife
- Long-term remediation technology (i.e. natural attenuation)
- Also called ecological restoration
- Society for Ecological Restoration
  - www.ser.org

Common starting conditions of a TE-polluted site

- Acid soil (but sometimes alkaline)
- Barren, no vegetation
- Poor in macronutrients (N,P,K and Ca) but sometimes high in Mg
- Poor in SOM
- ‘Dysfunctional’ soil microbiology
- Poor soil structure

Common steps to start a successful phytostabilization project

- Analyze the metal content and the soil physical/chemical characteristics
- Adjust the pH to neutral (add gypsum or lime)
- Add compost and organic amendments to supply N, P, K and S and normally required microelements in phytoavailable forms. Organic-N is especially valuable because it is slow-release and can persist long enough to support establishment of a living soil system
  - Anthyllis vermeraria appreciable metal tolerance (legume, N fixation)
- Choose adapted local species of tolerant or accumulator plants, drought-tolerant (?)

Mt. Belvidere, VT

- Revegetation of serpentine asbestos mine waste from northern Vermont.
- Need to establish vegetative cover to stop wind and water erosion of the asbestos to cause exposure of nearby communities
- Strong slope of the mine wastes
- The site has been barren since 1950

Belvidere Mountain Site, Vermont
Serpentine Asbestos Mine Wastes

Belvidere Mountain Site, Vermont
Serpentine Asbestos Mine Wastes

Installation of plots

- Remediation Amendment Mixture:
  - Compost (Intervale or Foster Farms) @80 T/A (180 t/ha)
  - Gypsum ($CaSO_4 \cdot 2H_20$) @ 25 T/A (56 t/ha)
  - Limestone @ 10 T/A (22 t/ha)
  - NPK Fertilizer equal to roadside reveg rate
- Seeding Mixture:
  - Perennial ryegrass
  - Tall fescue
  - Kentucky bluegrass
  - Alsike clover with rhizobium

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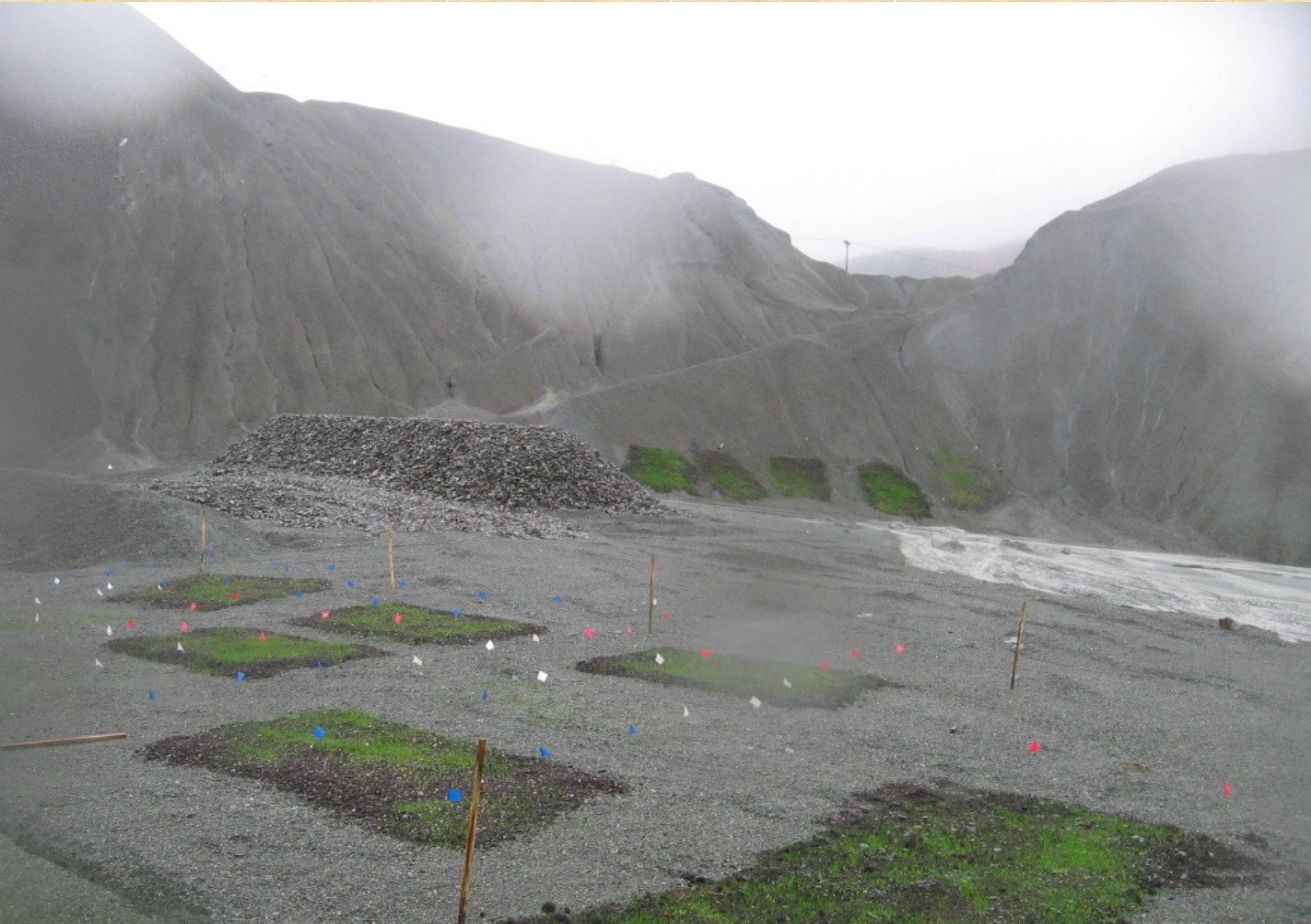
Test plots with two compost mixtures vs. control .

Cover crops establishment



Sampling Block 2 (Intervale Farms Compost)

Test plots at VAG on strong slope

Rooting well into mineral layer below top-dressed compost.

Rooting well into mineral layer below top-dressed compost.

Mt. Belvidere, VT

- Rock is serpentine, rich in Ni, Cr, Co, Fe, Mn, and Mg silicate. Deficient in many plant nutrients (P, Ca, N, K). Nearly lacks soil OM and microbes.
- Extremely infertile; Mg phytotoxic=Ca deficient.
- Not Ni-, Co-, or Cr-phytotoxic due to high pH (>8.0) which is caused by presence of Mg-silicate.
- Alternative to *in situ* phytostabilization would be covering mine waste with 12-24 inches of topsoil!

Phytomining

Nickel provides the best example for using natural hyperaccumulator plants to phyto-extract soil Ni for profit.

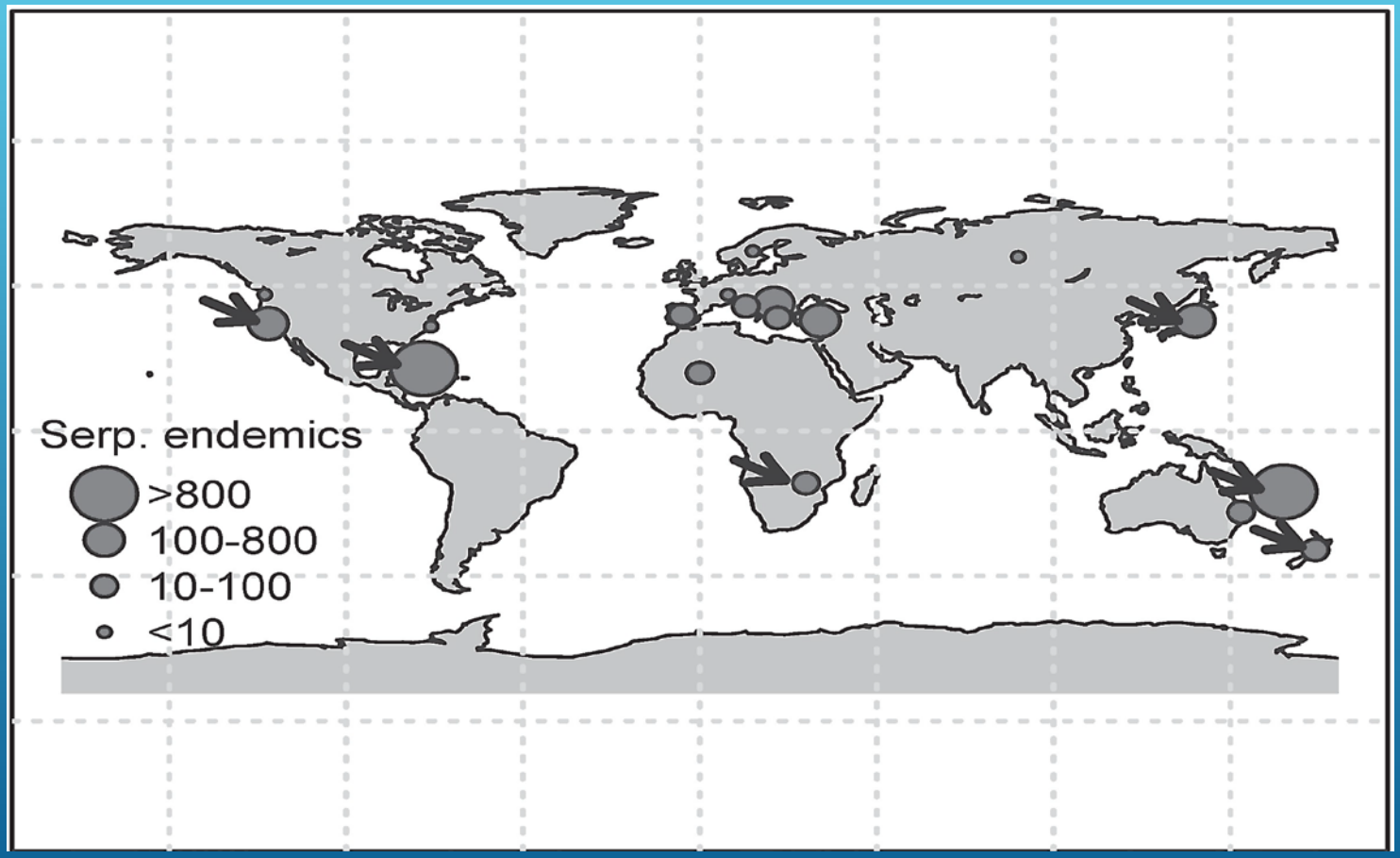
Dried plant material of hyperaccumulators grown on Ni-rich serpentine soil is reduced to an ash and the metal is recovered using conventional metal refining methods, such as acid dissolution or electrowinning.

Sub-or low-grade ores contain concentration of target metal below the content required to be economically extracted and smelted by conventional methods.

Most of these ore bodies are associated with ultramafic deposits that generate serpentine soils after weathering of the ultramafic rocks.

Serpentine soils

A distinctive vegetation has evolved on serpentine soils



Map of the worldwide distribution of serpentine endemic diversity in 18 of the world's serpentine-containing regions. (from Anacker, 2010).

Serpentine soils

Serpentine soils:

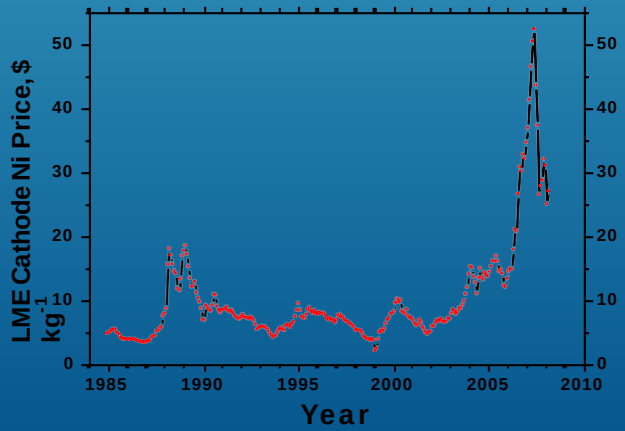
- low availability of Ca relative to Mg
- deficiency of essential macronutrients
- high levels of potentially phytotoxic heavy metals (Ni, Cr, Co, Mn).

Test field on Brockman gravelly loam in Josephine Co., OR

Alyssum for Ni Phytomining

Field of flowering *Alyssum murale* near Cave Junction on serpentine soil, Oregon, USA.

Ash from incineration of biomass of *Alyssum* shoots grown on field plots on Oregon serpentine soils.



Ni phytomining is highly profitable.

High-grade Ni ore ready for smelter processing.

Goal: increase phytoextraction efficiency

- ❑ Identify production practices to maximize profit
- ❑ Use plant breeding methods to combine high Ni accumulation and high harvestable yield
- ❑ Evaluate methods to maximize metals in biomass

Mowing *Alyssum murale* using farm equipment

Yin Li making crosses between *Alyssum murale* genotypes in Field, 1997

Phytomining

Pros

- Profitable agricultural industry, considering the low productivity of serpentine soils and the high value of Ni that can be annually phytomined.
- Much less disruptive of the land than strip mining lateritic serpentine' deposits.
- Bio-ore contains higher Ni concentration (6-16%) than normal Ni ores and free of Mn, Fe, and Si oxides as in conventional ores

Cons

- To be economically viable, phytomining should be able to produce about \$500 ha^{-1}, and most phytomining operations can gain additional revenue from incineration of biomass to generate electricity.
- A critique related to the environmental sustainability of phytomining addresses the efficiency of phytomining relative to conventional mining

Environmental sustainability of phytomining: Critique

- Phytomining of surface serpentine soil will take between 3 to 18 crop cycles before the surface Ni is depleted and the surface soil needs to be removed to continue phytomining of the deeper soil layers.
- Concerns about the introduction of a monoculture of possibly exotic species and disruption of serpentine ecosystem and native endemic flora.

Environmental sustainability of phytomining: Support

- Environmental impact similar to that of commercial farming. Phytomining is considered to have a positive effect of soil erosion by the effect of plant roots relative to the open pit and the 'desert-like' landscape left after conventional mining operation has ceased, and substantial site remediation is required at the end of the mine.
- Phytomining, instead, can improve the quality of the soil for post-mining operation over the duration of the phytomine. It is necessary, however, to study the potential environmental impacts of the phytomine during the planning phase and before the phytomining operation is set in place.
- Hence, this technology requires a team of expert agronomists, ecologists, and soil scientists to carefully choose the proper species for phytoextraction of particular a metal.

Environmental sustainability of phytomining: Support

- Various steps can be taken to reduce the ecological risks associated with monoculture and introduction of potential exotic species. For example: 1) analysis of phytoextraction potential of native vegetation and selection of the best-performing native species for metal extraction efficiency, 2) adoption of principles of agro-ecology, such as cultivation of combination of various native species, and 3) use of alternative fertilizers (sewage sludge biosolids) and bio-herbicides.

Environmental sustainability of phytomining: Support

- Fertility of land is likely to be increased after phytomining operation because of increased root and microbial activity in the soil profile, Ni removal, and pH and fertility management.
- Therefore, landholders may want to use land for food production after phytomining has reached Ni depletion of the top layers and, therefore, reduced Ni toxicity to crops occurs.
- The possibility of restoring serpentine soils post-phytomining and convert those soils to food production is an important aspect of environmental sustainability of phytomining and needs to be addressed in future studies.

Physiological mechanisms of root uptake

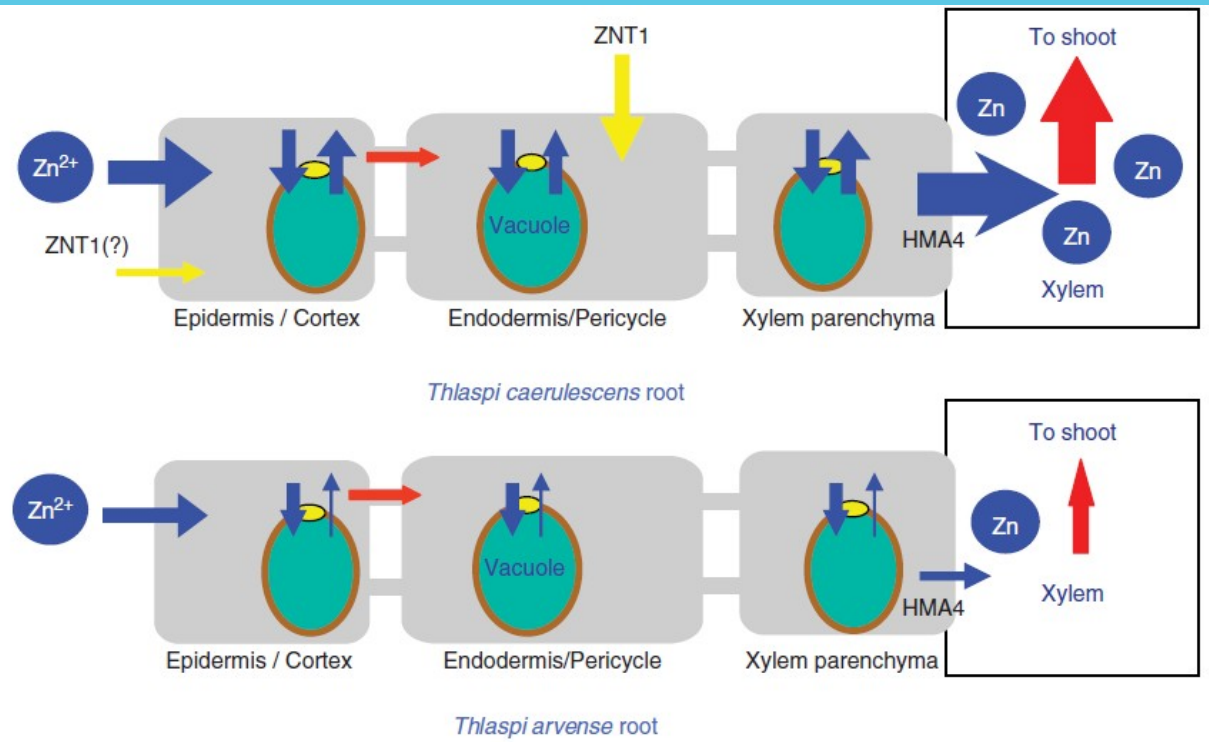


FIG. 1. Model of Zn transport into and across the root of *T. caerulescens*. The model depicts some of the aspects of and differences in the movement of Zn^{2+} from the soil into and across the root of *T. caerulescens* compared with *T. arvense*, with several possible candidate transporters indicated at specific transport steps. For uptake of Zn from the soil into the root epidermis/cortex, *T. caerulescens* exhibits elevated levels of influx across the root-cell plasma membrane compared with *T. arvense*. Previous speculation in the literature suggested TcZNT1 may be the transporter facilitating this uptake, but recent localization of the Arabidopsis homologue of the *TcZNT1* gene suggests it may actually be more involved in metal loading into the stele (see Fig. 4). Hence ZNT1-mediated Zn uptake into the epidermis is marked with a question mark, and it is also shown that ZNT1 may be mediating Zn uptake from the apoplast into cells of the pericycle and other cells within the stele, The model also indicates there is less vacuolar sequestration of Zn in roots of *T. caerulescens*, which would keep more of the absorbed Zn in a mobile pool moving radially through the endodermis and pericycle to the xylem parenchyma. Zn is then believed to be loaded into the xylem vessel elements via the ATPase, HMA4, for subsequent transport to the shoots. Blue and yellow arrows denote Zn transport across membranes, while red arrows denote Zn transport in symplasm or the apoplasm (xylem vessels).

Physiological mechanisms of root-to-shoot transport

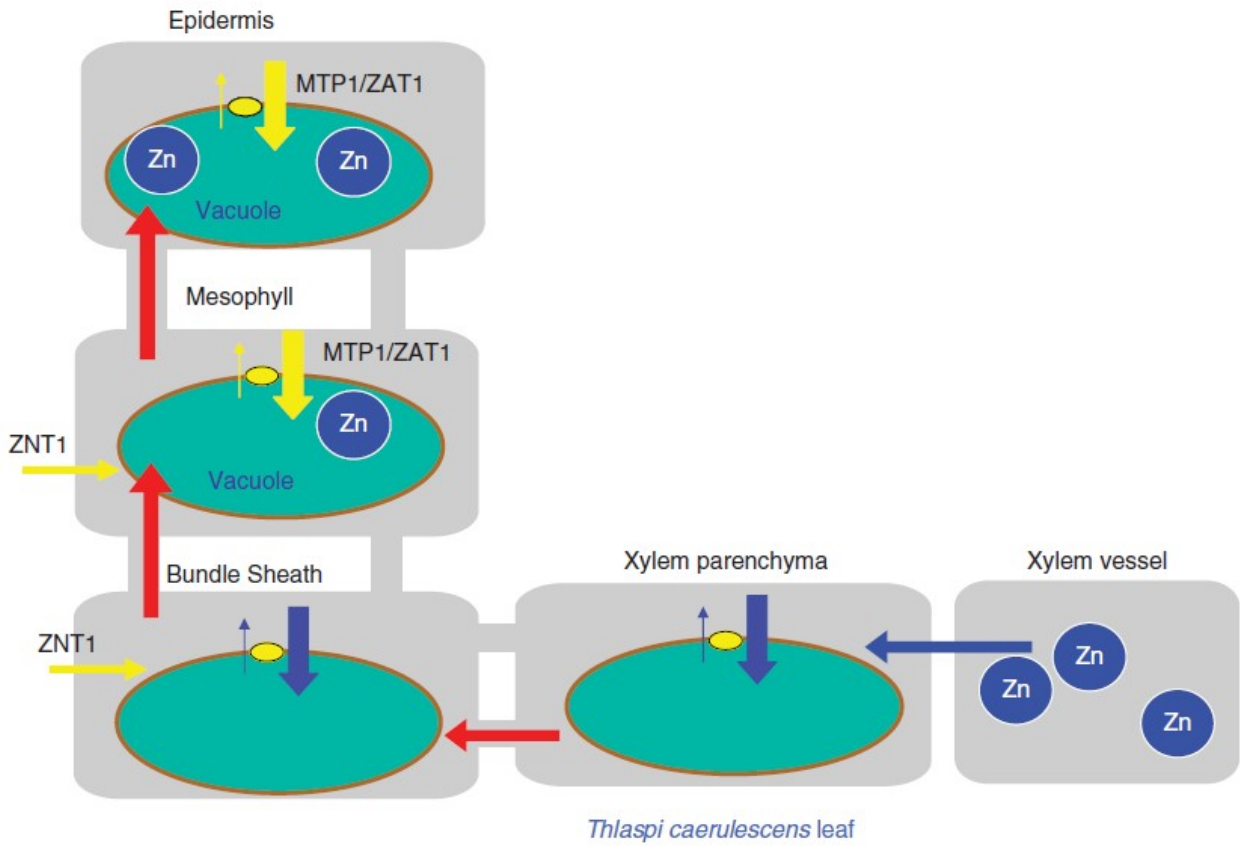


FIG. 2. Model of Zn transport and storage in the leaf. The model depicts Zn transport in the leaf from the xylem vessel through xylem parenchyma and bundle sheath cells to the sites of leaf storage, the leaf mesophyll and epidermis. Based on cellular expression studies in leaves of *T. caerulescens*, we suggest ZNT1 may be the transporter facilitating uptake into bundle sheath and mesophyll cells from the leaf apoplast. How Zn ultimately is loaded into epidermal cells is not known. Here we suggest that the transporter, MTP1/ZAT1, may facilitate vacuolar sequestration of metals in mesophyll and epidermal cells. Blue and yellow arrows denote Zn transport across membranes, while red arrows denote Zn transport in symplasm.

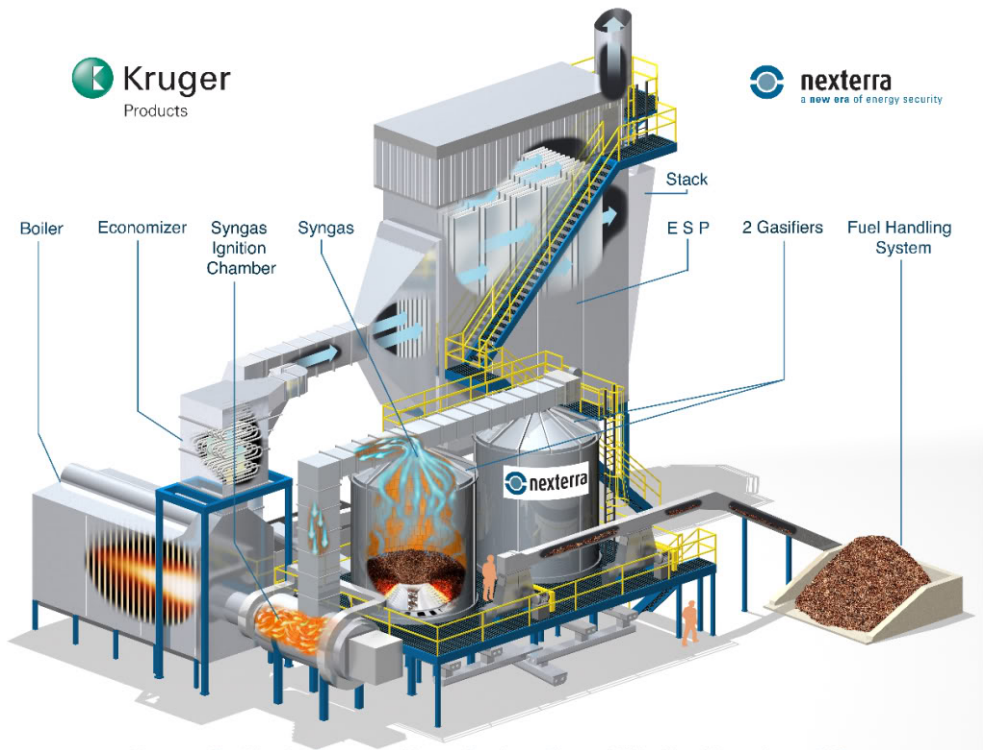
At least three processes make a major contribution to the ability to hyperaccumulate/hypertolerate metals:

- Enhanced root uptake and loading into the xylem
- Superior root-to-shoot translocation
- Efficient detoxification via chelation and sequestration, predominantly within leaf cell vacuoles

Nickel in the environment

- A component of plant urease and accepted as an essential ultra-micronutrient
- Nickel occurs naturally in the environment at low levels (except for calamine and serpentine soils)
- Some Ni deficiency in pecan

Trace element laden plant material will be used in gasifier to produce bioelectricity.



Nexterra Gasification System at Kruger Products Tissue Mill in New Westminster B.C.

Metal homeostasis - ligands

In leaf and shoots:

- Organic acids: Citric and malic acid

In the xylem sap:

- S-containing ligands (phytochelatins, metallothioneins)
- Amino acids (Histidine)
- Or just free hydrated cations

The case of Cd

- Cd has a great potential to escape the soil-plant barrier
- It has low affinity for metal-sorbing phases (oxides, SOM) and is readily translocated to shoots at high levels before phytotoxicity is observed.

Ecological risk assessment

Ecological risk assessment includes three phases, and is generally conducted following the ***Guidelines for Ecological Risk Assessment*** (U.S. EPA, 1998). www.epa.gov/risk_assessment/ecological-risk.htm

- **Planning - Planning and Scoping process**
  EPA begins the process of a Ecological risk assessment with planning and research.

- **Phase 1 - Problem formulation**
  Information is gathered to help determine what, in terms of plants and animals, is at risk and what needs to be protected.

- **Phase 2 - Analysis**
  This is the determination of what plants and animals are exposed and to what degree they are exposed, and if that level of exposure is likely or not to cause harmful ecological effects.

- **Phase 3 - Risk characterization**
  Risk characterization includes two major components: risk estimation and risk description. "Risk estimation" combines exposure profiles and exposure-effects. "Risk description" provides information important for interpreting the risk results and identifies a level for harmful effects on the plants and animals of concern.

Bioaccumulation Definitions

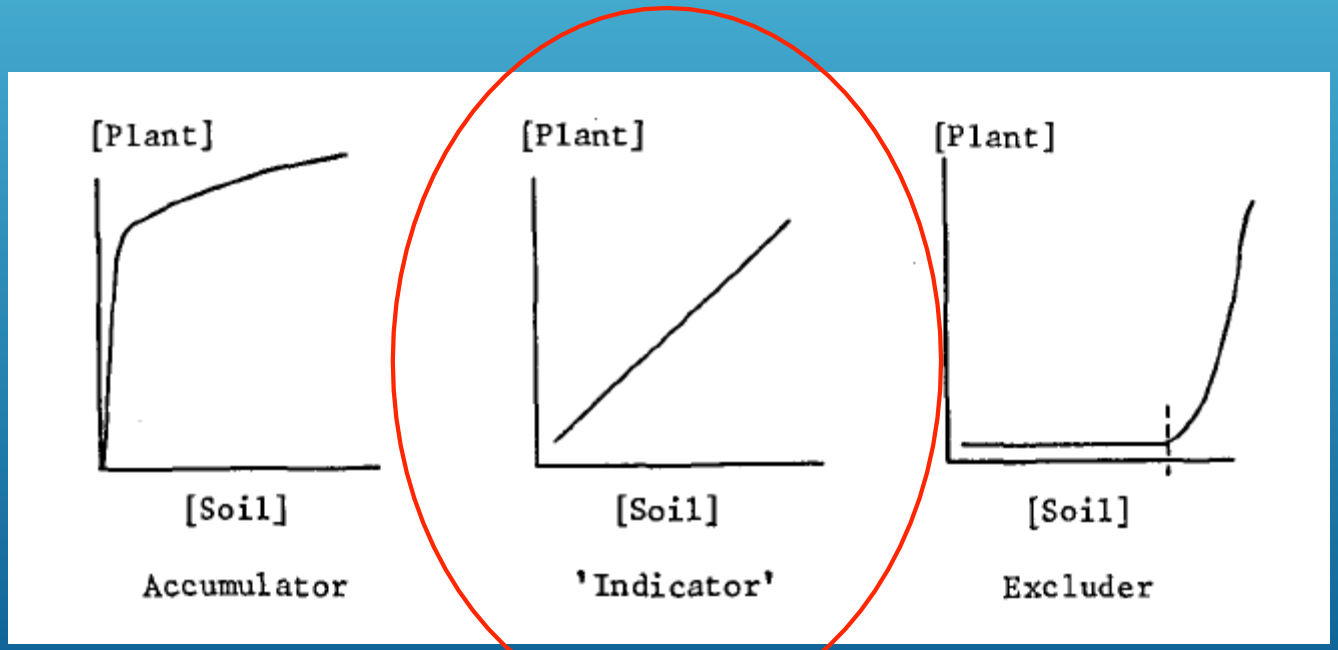
- ***Bioaccumulation*** – "The biological sequestering of a substance at a higher concentration than that at which it occurs in the surrounding environment or medium." - U.S. Geological Survey, 2007
- ***Bioaccumulation*** – "General term describing a process by which chemicals are taken up by an organism either directly from exposure to a contaminated medium or by consumption of food containing the chemical." – U.S. Environmental Protection Agency, 2010
- ***Bioaccumulation*** – "Bioaccumulation is defined as the accumulation of chemicals in the tissue of organisms through any route, including respiration, ingestion, or direct contact with contaminated water, sediment, and pore water in the sediment." – U.S. Environmental Protection Agency, 2000
- ***Bioaccumulation*** – "Progressive increase in the amount of a substance in an organism or part of an organism which occurs because the rate of intake exceeds the organism's ability to remove the substance from the body." – International Union of Pure And Applied Chemistry, 1993

Bioindication/biomonitoring

- Indicator species are organisms that serve as a measure of the environmental conditions that exist in a given environment. These may be various animal and plant organisms and their organs or products.

Indicators

- Where uptake and transport of metals to the shoot are regulated so that internal concentration reflects external levels



Characteristics of an ideal indicator

- Suitable accumulation rate of some or selected TE
- Toxitolerance with no sensitivity to the accumulating element
- Present in large amounts in the ecosystem under investigation
- Wild distribution in various environments, and wild geographic range
- Easy to identify and sample
- No seasonal differences in availability and applicability
- Existence of a correlation between accumulation and input to the ecosystem

Most common bioindicators

- Dandelion
- Mushrooms (Se, Cu, Zn)
- Nettle (metals)
- Mosses (air pollution)
- Lichens (air pollution)

Alyssum and Ni

- *Alyssum* species are Ni hyperaccumulators and can be grown on serpentine soils (Ni-rich soils) to extract the Ni as bio-ore
- This process is called phytomining, green-approach to mining where hyperaccumulator plants can be used to extract the metal from the earth; it can be applied to Co if we find good Co hyperaccumulators

Engineering methods pros and cons

PROS

- Fast cleanup
- Secure a complete removal of TE

CONS

- Very expensive
- Destructive of soil environment (physical and chemical and microbiological properties)
- Not sustainable and not environment friendly

Green-technologies pros and cons

PROS

- Solar-driven; no energy costs
- Cheap to install and manage (as costly as growing crops)
- Accepted by the public, sustainable, restoring the ecosystem

CONS

- Slow cleanup
- Context dependent, plants adapted to certain climatic conditions

Induced phytoextraction

- Pb = addition of metal chelators (EDTA, DTPA, etc.) to the soil to chelate the metal and induce higher plant phytoextraction is not economically viable and environmentally sustainable
- Au = induced phytoextraction of gold is successful because it is operated with thiocyanate, and Au is irrigated with it on a plastic membrane to prevent leachate loss and to promote Au uptake by plants

***Alyssum* for phytomining**

Mt. Belvidere, VT

- Rock is serpentine, rich in Ni, Cr, Co, Fe, Mn, and Mg silicate. Deficient in many plant nutrients (P, Ca, N, K). Nearly lacks soil OM and microbes.
- Extremely infertile; Mg phytotoxic=Ca deficient.
- Not Ni, Co, or Cr phytotoxic due to high pH (>8.0) which is caused by presence of Mg-silicate.
- Alternative to *in situ* phytostabilization would be covering mine waste with 12-24 inches of topsoil!

Bioavailability and bio-accessibility

The term “environmentally available fraction” refers to the portion of total metal in soil, sediment, water, or air that is available to contact or enter an organism, can be absorbed by plants.

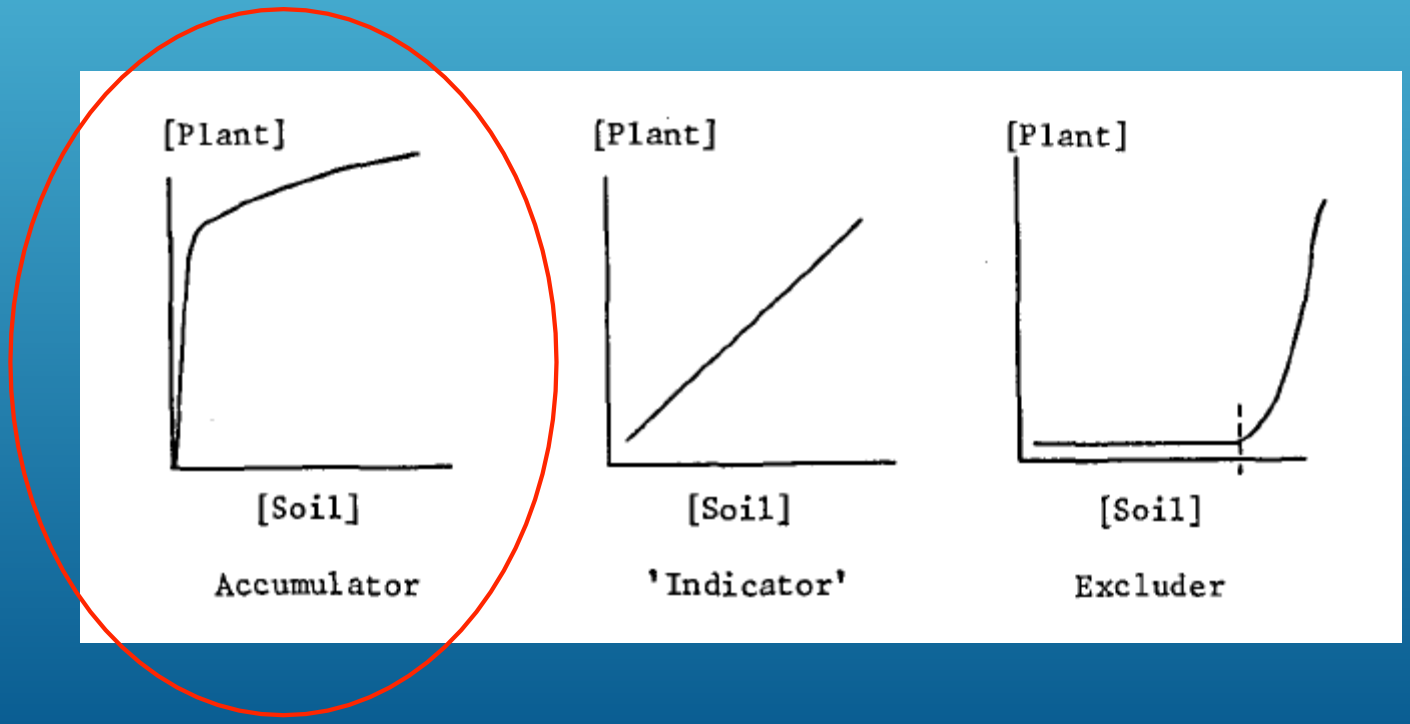
Of that portion, the bioaccessible fraction (BF) is the amount that actually interacts at the organism’s contact surface and is potentially available for absorption or adsorption (metals cross biological membranes).

Bioavailability/Hazard Relationship

If two substances were equally toxic at comparable levels of target organ exposure, the substance with the higher bioavailability would pose the greatest risk.

Accumulators

- Where metals are concentrated in above-ground plant parts from low to high soil levels



TE deficiencies affect most of world's population

- 2 billion suffer from anemia-Fe deficient
- 35% of children between 0-5 yrs suffer from Zn and Fe deficiency
- Almost 1 billion suffer from I and Se deficiency