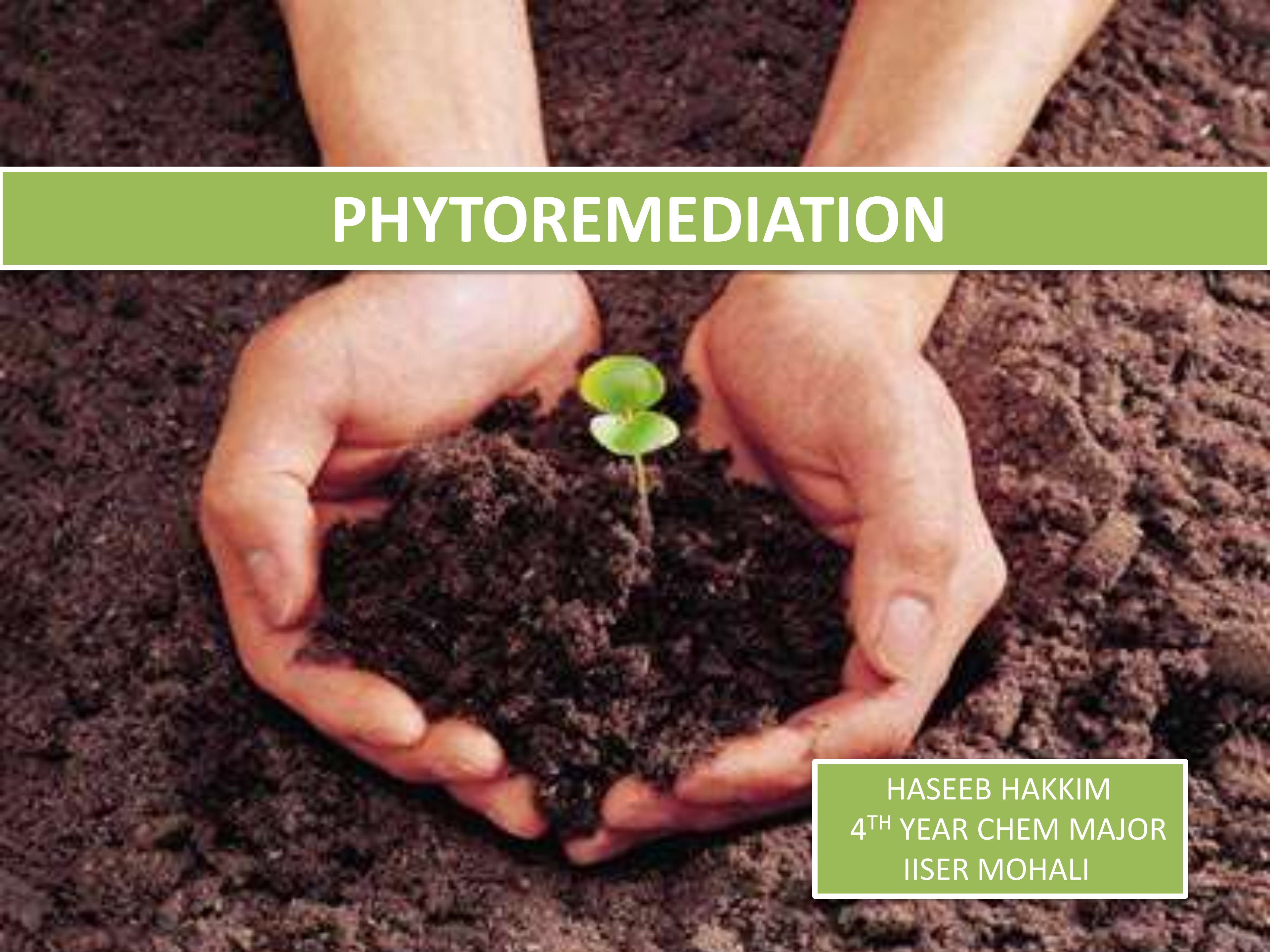

PHYTOREMEDIATION

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4TH YEAR CHEM MAJOR
IISER MOHALI

OUTLINE

- DEFINITION
- THE IMPORTANCE OF PHYTOREMEDIATION
- MECHANISM BEHIND THE REMEDIATION PROCESS
- APPLICATIONS
- THE ROLE OF BIOTECHNOLOGY
- CONCLUSION
- REFERENCES

PHYTOREMEDIATION

Phytoremediation is the use of plants to clean up a contamination from soils, sediments, and water. Phytoremediation takes the advantage of the unique and selective uptake capabilities of plant root systems, together with the translocation, bioaccumulation, and contaminant degradation abilities of the entire plant body for the remediation process. This technology is environmental friendly and potentially cost effective.

► Phyton = Plant (in Greek) & Remediare = To remedy (in Latin).

SOIL POLLUTION

Soil Pollution is defined as the build-up in soils of persistent toxic compounds, chemicals, salts, radioactive materials, or disease causing agents, which have adverse effects on plant growth and animal health. It is caused by the presence of xenobiotic (human-made) chemicals or other alteration in the natural soil environment.

The most common chemicals involved are petroleum hydrocarbons, polynuclear aromatic hydrocarbons (such as naphthalene and benzo(a)pyrene) , solvents, pesticides, lead and other heavy metals .

The soil close to Yangzong Lake, southwest China's Yunnan Province was seriously polluted by Arsenic in 2009.

HEAVY METALS

Heavy metals are metallic chemical elements having atomic weight between 63.54 and 200.59 , and a specific gravity greater than about 5.0 g/cc. They are toxic, can damage living things at low concentrations and tend to accumulate in the food chain. The most common heavy metal contaminants are : As , Cd , Cr, Cu , Hg , Pb, and Zn .

Chronic problems associated with long-term heavy metal exposures are:

- Lead – mental lapse.
- Cadmium – affects kidney, liver, and GI tract.
- Arsenic – skin poisoning, affects kidneys and central nervous system.

High levels of metals in soil can be phytotoxic. Poor plant growth and soil cover caused by metal toxicity can lead to metal mobilization in runoff water and subsequent deposition into nearby bodies of water. Furthermore, bare soil is more susceptible to wind erosion and spreading of contamination by airborne dust.

SOURCES OF HEAVY METALS IN THE ENVIRONMENT

- Manufacturing, and the use of synthetic products like pesticides, paints, batteries.
- Municipal and industrial waste .
- Mining waste.
- Accidental Spills.
- Sediment from waste water treatment plant.
- Leachate from solid waste treatment plant.
- Acid rain.
- Nuclear wastes.

Industrial waste

Oil spill

Sediment from solid waste

Mining waste

REGULATORY LIMITS FOR HEAVY METALS

Table 5. Soil concentration ranges and regulatory guidelines for some toxic metals

Metal	Soil concentration range[a] (mg kg^{-1})	Regulatory limits[b] (mg kg^{-1})
Pb	1.00-6,900	600
Cd	0.10-345	100
Cr	0.05-3,950	100
Hg	<0.01-1,800	270
Zn	150.00-5,000	1,500

[a)] Riley *et al.*, 1992

[b)] Nonresidential direct contact soil cleanup criteria (NJDEP, 1996)

THE MOST IMPORTANT DISASTERS WITH HEAVY METALS

- Minamata Disaster
- Sandoz Chemical Spill
- Spanish Waste Water Spill
- Itai-Itai Disease

In 1952, the first incidents of mercury poisoning appear in the population of Minimata Bay in Japan, caused by consumption of fish polluted with mercury, bringing over 500 fatalities.

▶ Minamata Disaster

In 1932 Minamata Sewage containing mercury is released by Chisso's chemicals works into Minimata Bay in Japan. The mercury accumulates in sea creatures, leading eventually to mercury poisoning in the population .

▶ Sandoz Chemical Spill

The Sandoz chemical spill was a major environmental disaster on November 1, 1986 caused by a fire at a chemical factory Sandoz near Basel, Switzerland, sending tons of toxic chemicals into the nearby river Rhine and turning it red. The chemicals caused a massive mortality of wildlife downstream, killing among other things a large proportion of the European eel population in the Rhine, although the situation subsequently recovered within a couple of years. The stored chemicals included, beside urea and fluorescent dye, organophosphate insecticides, mercury compounds and organochlorides.

▶ Spanish Waste Water Spill

On April 25th, 1998, the dam of the mining residual tank of a pyrite mine in Aznalcollar, Spain, ruptured, releasing sludge and contaminated wastewater. The wastewater entered the Guadiamar River, polluting it with heavy metals like cadmium, lead, zinc and copper. The river pollution caused devastation to cultivated lands and forests. Harvests were no longer fit for consumption, causing financial problems for farmers in the area. Fish stocks were wiped out as well, and a number of birds died from consuming the polluted fish.

▶ Itai-Itai Disease

Itai-itai disease was the documented case of mass cadmium poisoning in Toyama Prefecture, Japan starting around 1912. The cadmium was released into rivers by mining companies in the mountains. The cadmium poisoning caused softening of the bones and kidney failure. The mining companies were successfully sued for the damage. Itai-itai disease is known as one of the Four Big Pollution Disease of Japan.

TRADITIONAL TREATMENTS FOR SOIL CONTAMINATION

Traditional treatments for metal contamination in soils are expensive and cost prohibitive when large areas of soil are contaminated. Treatments can be done in situ (on-site), or ex situ (removed and treated off-site). Both are extremely expensive. Some treatments that are available include:

Table 1. Cost of soil treatment (Glass, 1999a)

Treatment	Cost ($/ton)	Additional factors/expenses
Vitrification	75-425	Long-term monitoring
Landfilling	100-500	Transport/excavation/monitoring
Chemical treatment	100-500	Recycling of contaminants
Electrokinetics	20-200	Monitoring
Phytoextraction	5- 40	Monitoring

Once metals are introduced and contaminate the environment, they will remain. Metals do not degrade like carbon-based (organic) molecules. The only exceptions are mercury and selenium, which can be transformed and volatilized by microorganisms. However, in general it is very difficult to eliminate metals from the environment.

PHYTOREMEDIATION

Because biological processes are ultimately solar-driven, Phytoremediation is on average tenfold cheaper than engineering-based remediation methods such as soil excavation, soil washing or burning, or pump-and-treat systems.

Phytoremediation is usually carried out *in situ* contributes to its cost-effectiveness and may reduce exposure of the polluted substrate to humans, wildlife, and the environment.

Depending on the underlying processes, applicability, and type of contaminant, phyto-remediation can be broadly categorised as::

To Treat Organic Contaminants :

- **Phytodegradation**
- **Phytostimulation**
- **Phytovolatilisation**.

To Treat Metal Contaminants :

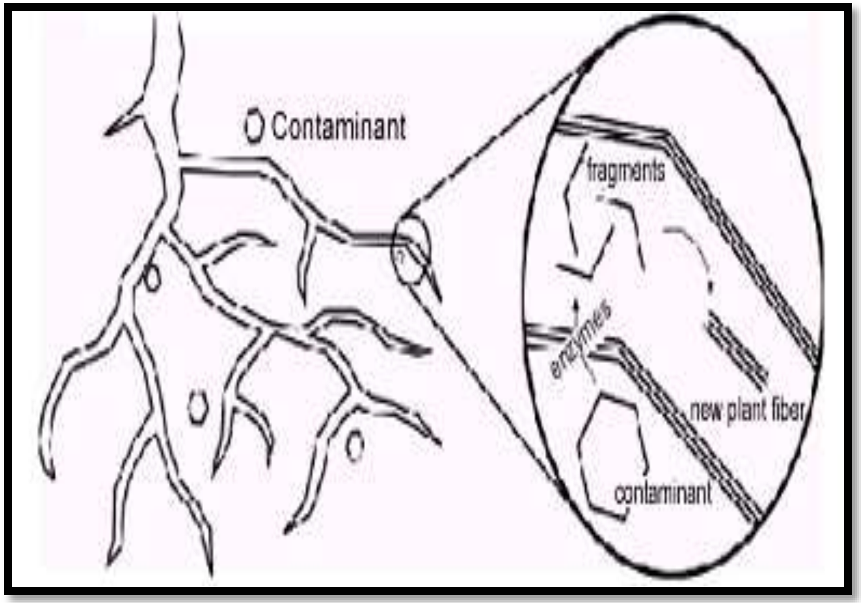
- **Phytoextraction**
- **Rhizofiltration**
- **Phytostabilisation**

The Use of Phytoremediation to Treat Organic Contaminants

► Phytodegradation

Phytodegradation, also called phyto-transformation, is the breakdown of contaminants taken up by plants through metabolic processes within the plant, or the breakdown of contaminants surrounding the plant through the effect of compounds (such as enzymes) produced by the plants. Complex organic pollutants are degraded into simpler molecules and are incorporated into the plant tissues to help the plant grow faster .

Plant enzymes used for the degradation include nitroreductases (degradation of nitroaromatic compounds), dehalogenases (degradation of chlorinated solvents and pesticides) and laccases (degradation of anilines). *Populus* species and *Myriophyllium spicatum* are examples of plants that have these enzymatic systems .



► Phytostimulation

• Phyto-stimulation also called Rhizodegradation or plant-assisted bioremediation /degradation, is the breakdown of contaminants in the rhizosphere (soil surrounding the roots of plants) through microbial activity that is enhanced by the presence of plant roots and is a much slower process than phytodegradation.

• Certain micro-organisms can digest organic substances such as fuels or solvents that are hazardous to humans and break them down into harmless products in a process called biodegradation. Natural substances released by the plant roots – sugars, alcohols, and acids – contain organic carbon that provides food for soil microorganisms and the additional nutrients enhance their activity.

► Phytovolatilisation

Phytovolatilisation is the uptake and transpiration of a contaminant by a plant, with release of the contaminant or a modified form of the contaminant from the plant to the atmosphere. Phytovolatilisation occurs as growing trees and other plants take up water and the organic contaminants. Some of these contaminants can pass through the plants to the leaves and evaporate, or volatilise, into the atmosphere. Poplar trees at one particular study site have been shown to volatilise 90% of the TCE they take up.

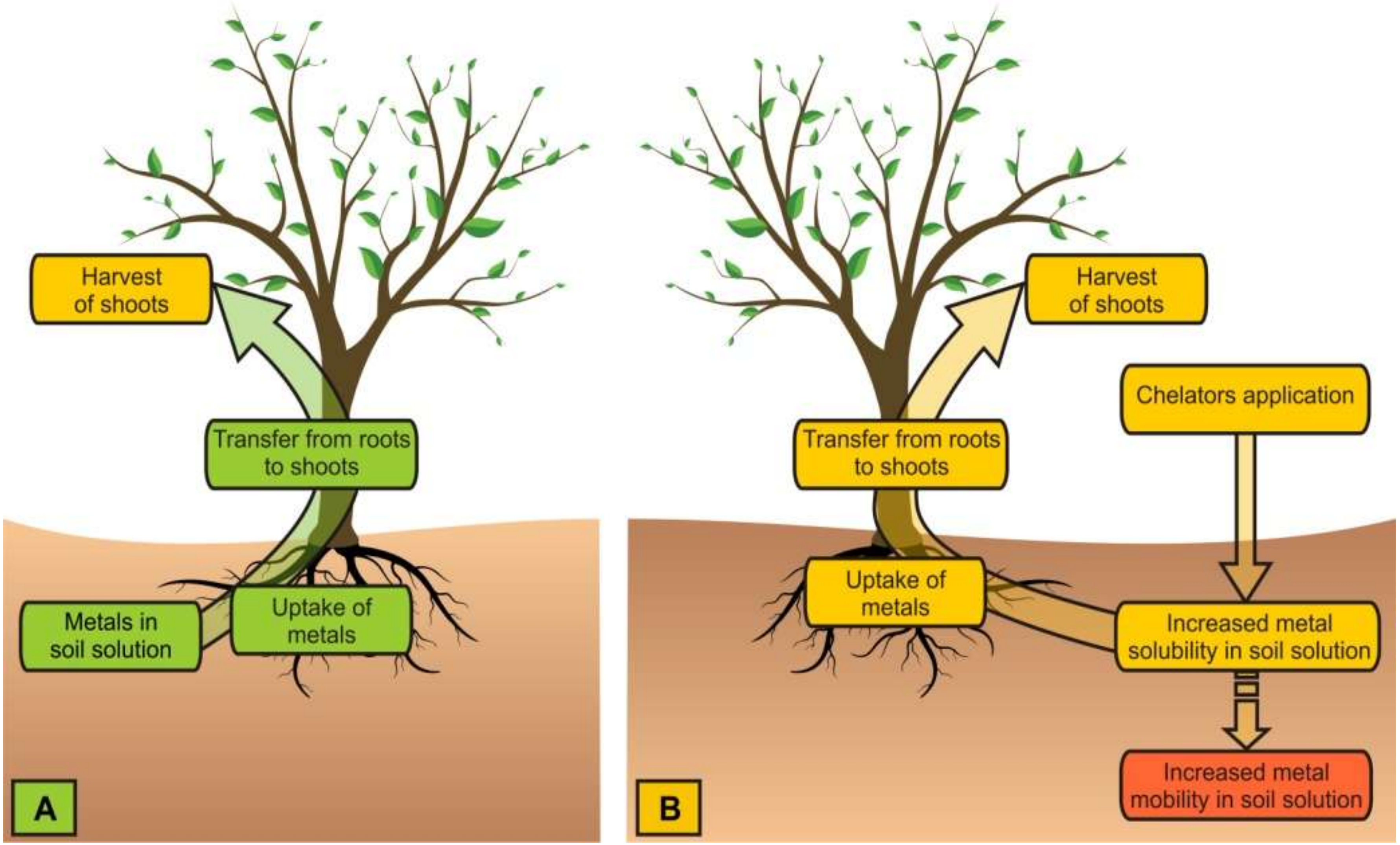
The Use of Phytoremediation to Treat Metal Contaminants

- **Phytoextraction**

Phytoextraction, or phytomining, is the process of planting a crop of a species that is known to accumulate contaminants in the shoots and leaves of the plants, and then harvesting the crop and removing the contaminant from the site.

The harvested plant tissue, rich in accumulated contaminant, is easily and safely processed by drying, ashing or composting.

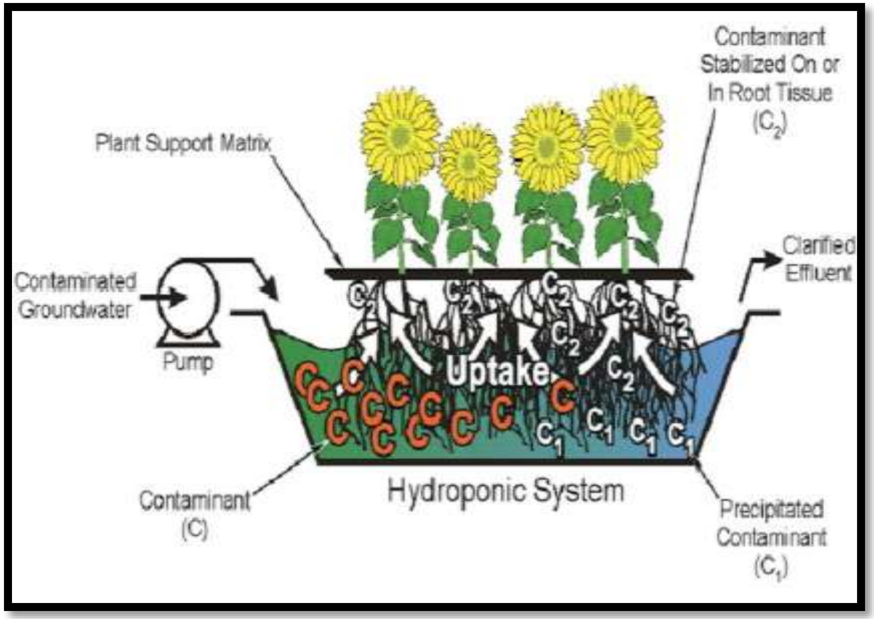
The potential for phytoextraction of several major metal contaminants including Pb is adversely affected by metal adsorption to soil solids and/or precipitation as insoluble compounds. Addition of synthetic chelates has been shown to stimulate the release of metals into soil solution and enhance the potential for uptake into roots. A variety of synthetic chelates have this potential to induce Pb desorption from the soil matrix. Their effectiveness, in decreasing order is EDTA > HEDTA >DTPA >EGTA >EDDHA. This is known as **Assisted Phytoextraction**.



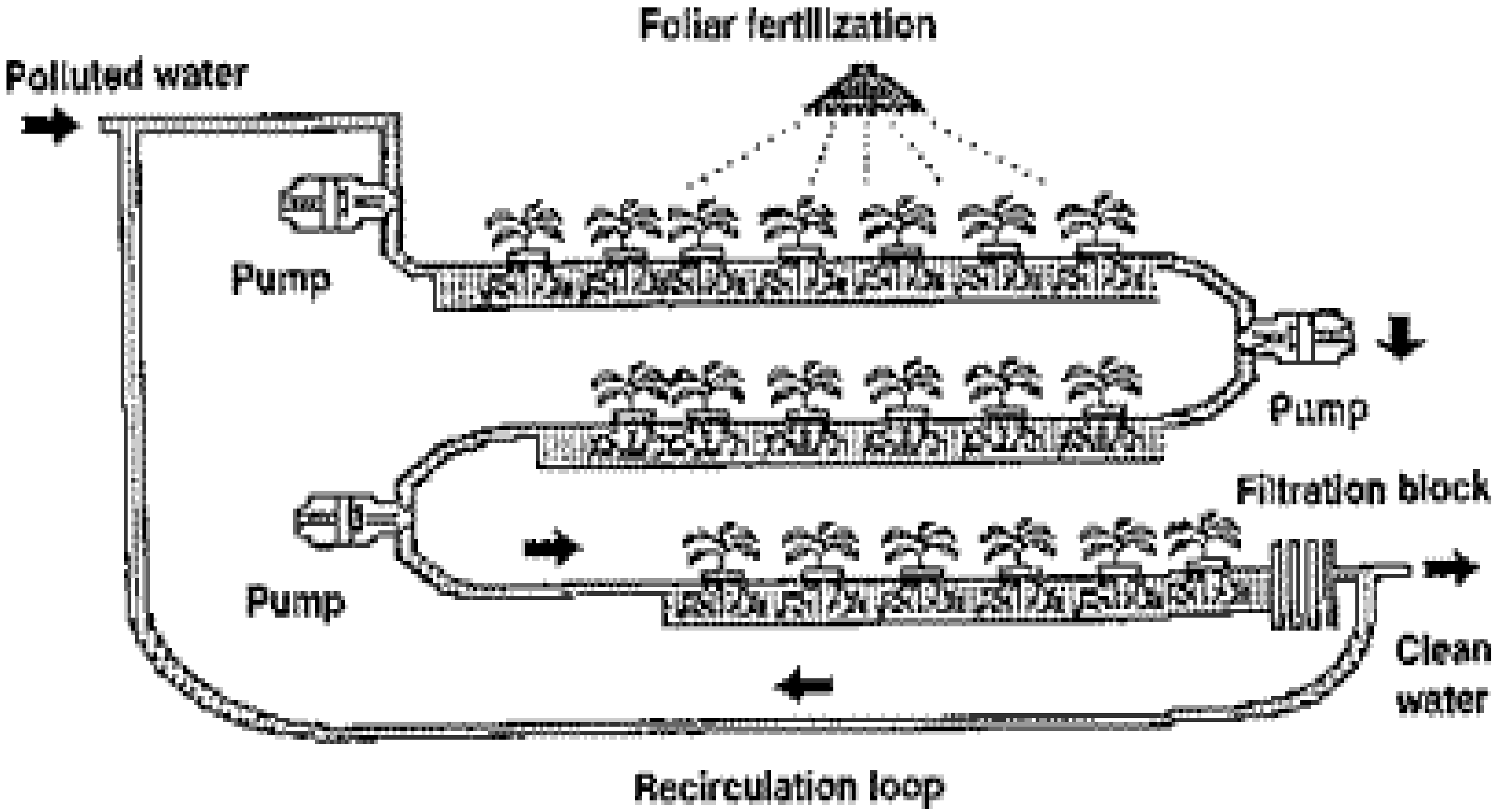
Schematic representation of the processes of natural (A) and assisted (B) phytoextraction.

► Rhizofiltration

Rhizofiltration ('rhizo' means 'root') is the adsorption or precipitation onto plant roots (or absorption into the roots) of contaminants that are in solution surrounding the root zone. Rhizofiltration is similar to phytoextraction, but the plants are used to clean up contaminated groundwater rather than soil.



For example, sunflowers were successfully used to remove radioactive contaminants from pond water in a test at Chernobyl, Ukraine.



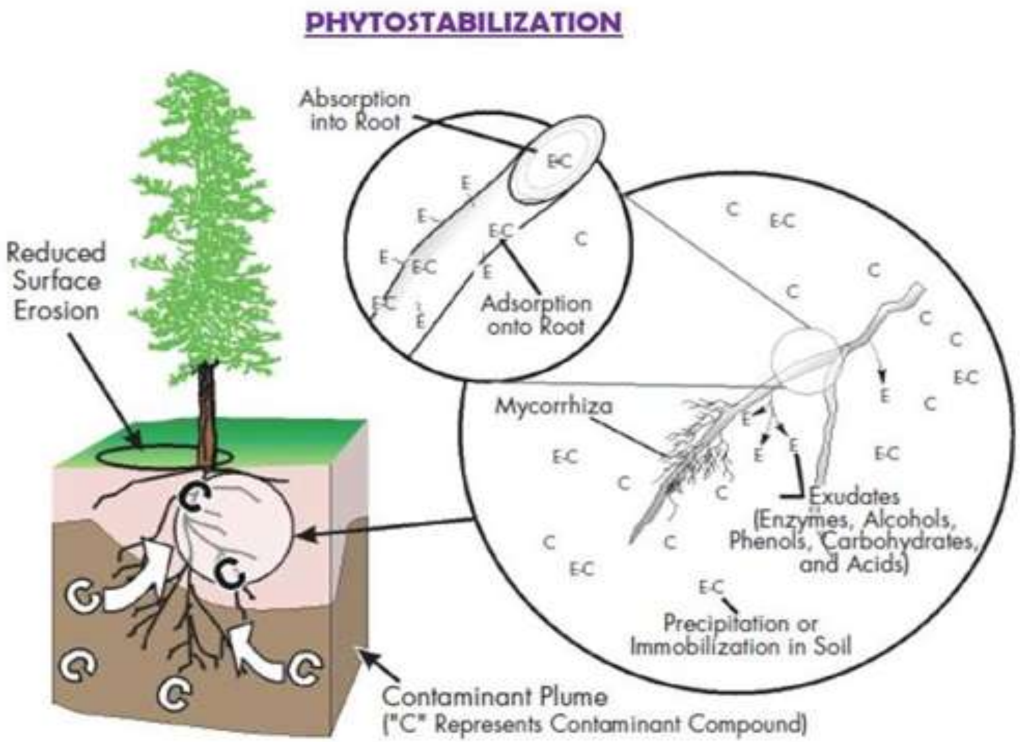
Contaminated water is either collected from a waste site and brought to the plants or the plants are planted in the contaminated area, where the roots then take up the water and the contaminants dissolved in it. As the roots become saturated with contaminants, they are harvested.

Plants with high root biomass, or high absorption surface, with more accumulation capacity (aquatic hyperaccumulators) and tolerance to contaminants achieve the best results. Promising examples include *Helianthus annus*,*Brassica juncea*, *Phragmites australis*, *Fontinalis antipyretica* and several species of *Salix* , *Populus*, *Lemna* and *Callitriche* .

Whitney Water Purification Facility, New Haven, Connecticut, USA .

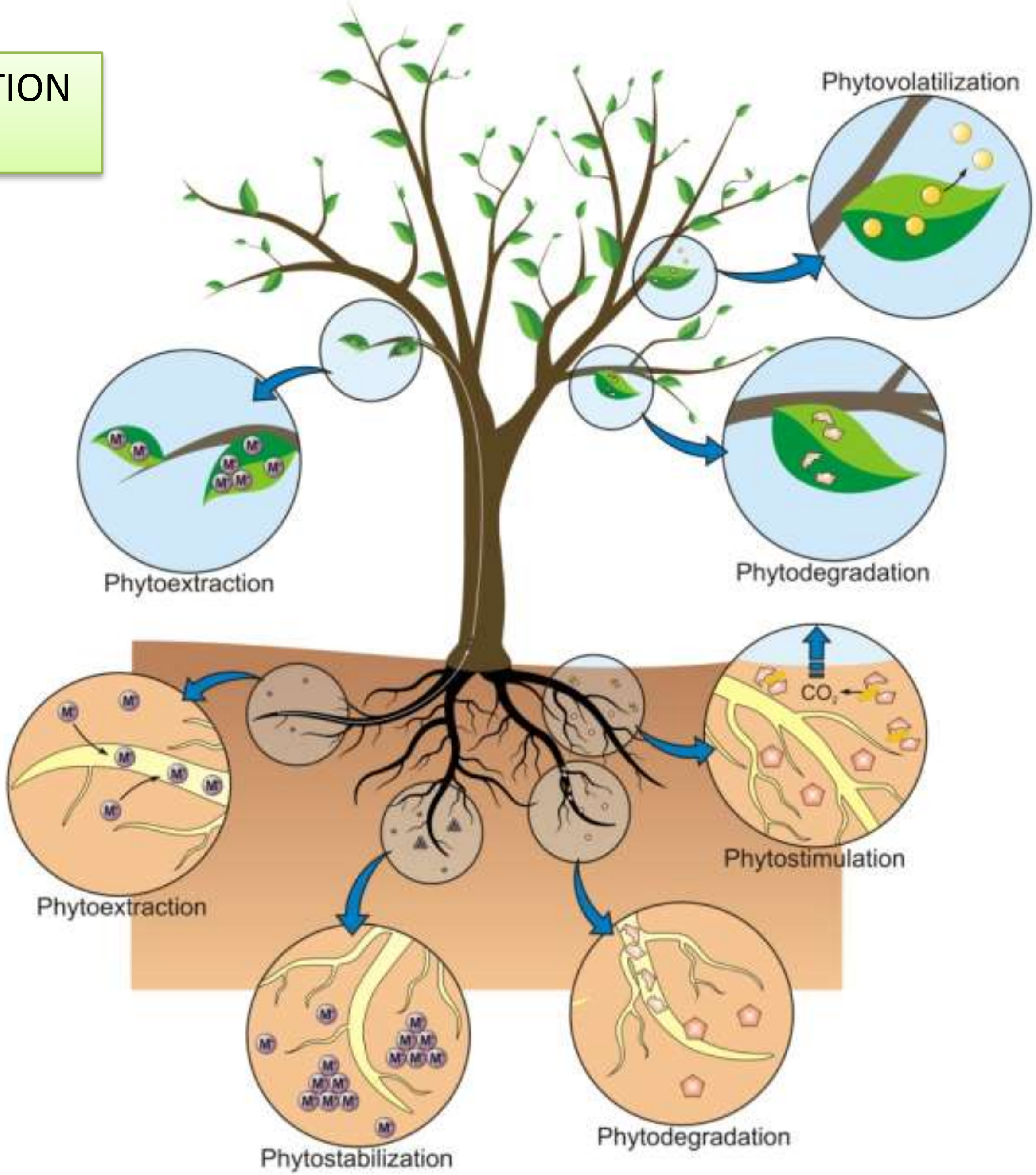
► Phytostabilisation

Phytostabilisation is the use of certain plant species to immobilise contaminants in the soil and groundwater through absorption and accumulation by roots, adsorption onto roots, or precipitation within the root zone of plants (rhizosphere). This process reduces the mobility of the contaminant and prevents migration to the groundwater or air, and also reduces bioavailability for entry into the food chain . This technique can be used to re-establish a vegetative cover at sites where natural vegetation is lacking due to high metal concentrations in surface soils or physical disturbances to surficial materials.



Metal-tolerant species can be used to restore vegetation to the sites, thereby decreasing the potential migration of contamination through wind erosion and transport of exposed surface soils and leaching of soil contamination to groundwater.

PHYTOREMEDIATION PROCESSES



BIOLOGICAL MECHANSM OF HEAVY METAL UPTAKE

The major processes involved in hyperaccumulation of trace metals from the soil to the shoots by hyperaccumulators include:

1. Bioactivation of metals in the rhizosphere through root-microbe interaction;

2. Enhanced uptake by metal transporters in the plasma membranes;

3. Detoxification of metals by distributing to the apoplasts like binding to cell walls and chelation of metals in the cytoplasm with various ligands, such as phytochelatins, metallothioneins, metal-binding proteins;

4. Sequestration of metals into the vacuole by tonoplast-located transporters.

► Hyperaccumulators are conventionally defined as species capable of accumulating metals at levels 100-fold greater than those typically measured in common non-accumulator plants.

Table 6. Several metal hyperaccumulator species and their bioaccumulation potential

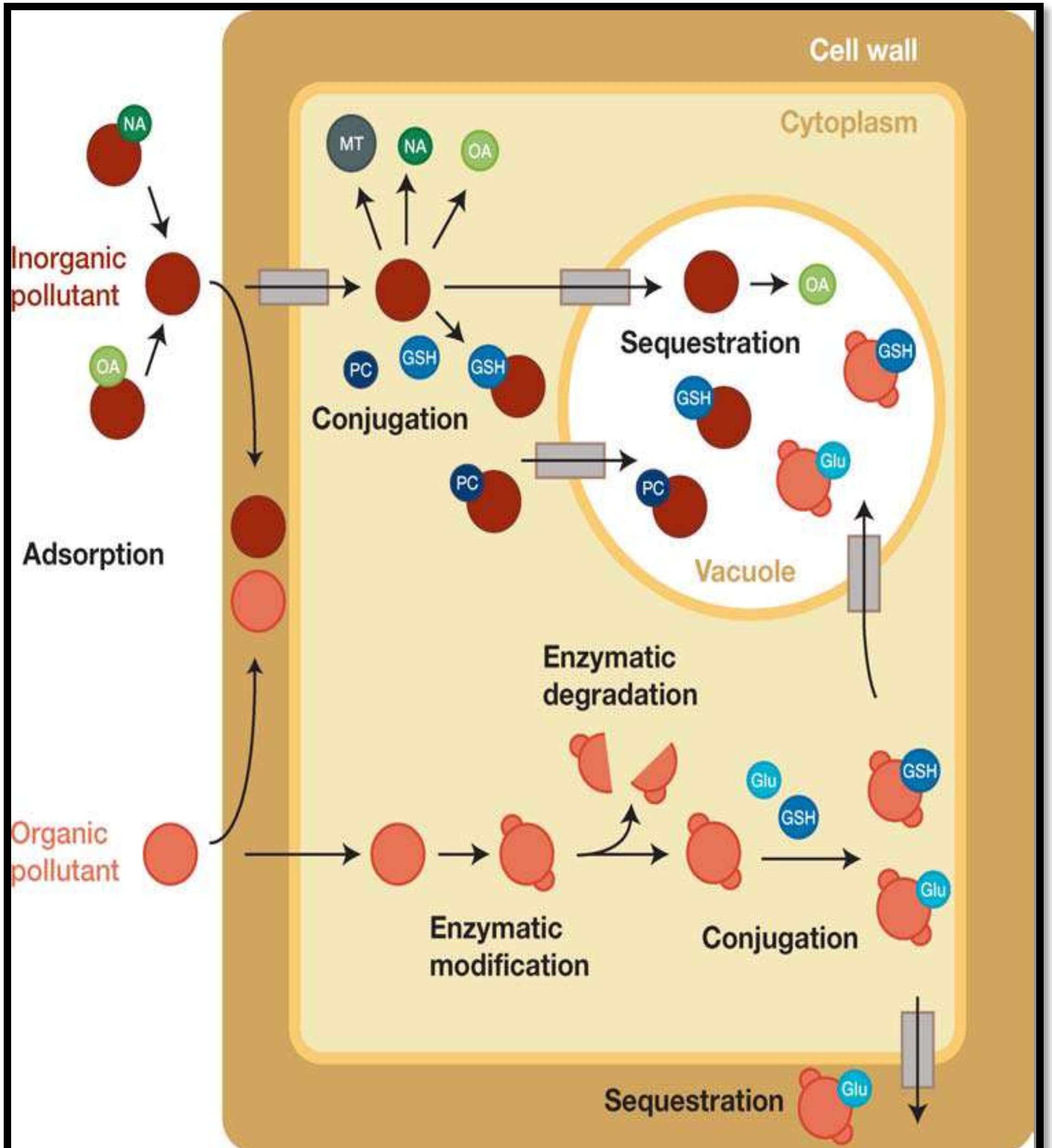
Plant species	Metal	Leaf content (ppm)	Reference
Thlaspi caerulescens	Zn:Cd	39,600:1,800	Reeves&Brooks(1983);Baker&Walker(1990)
Ipomea alpina	Cu	12,300	Baker&Walker (1990)
Haumaniastrum robertii	Co	10,200	Brooks (1977)
Astragalus racemosus	Se	14,900	Beath et al. (1937)
Sebertia acuminata	Ni	25% by wt dried sap	Jaffre et al. (1976)

Alyssum serpyllifolium

Thlaspi caerulescens

Brassica juncea

The ability to hyperaccumulate toxic metals compared to related species is because of their ‘Detoxification or Tolerance Mechanism’ .



Tolerance mechanisms for inorganic and organic pollutants in plant cells.

Detoxification generally involves conjugation followed by active sequestration in the vacuole and apoplast, where the pollutant can do the least harm. Chelators shown are

GSH: glutathione,

Glu: glucose,

MT: metallothioneins,

NA: nicotianamine,

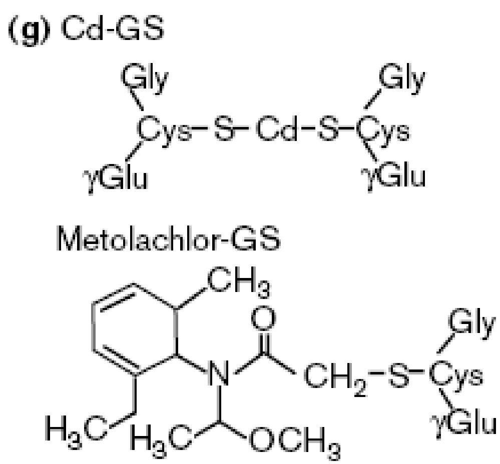
OA: organic acids (EX : mugenic and avenic acids)

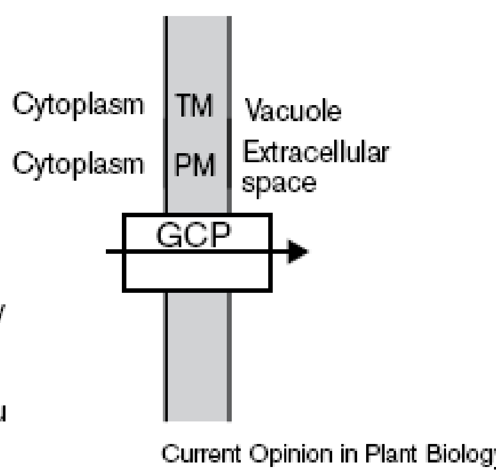
PC: phytochelatins.

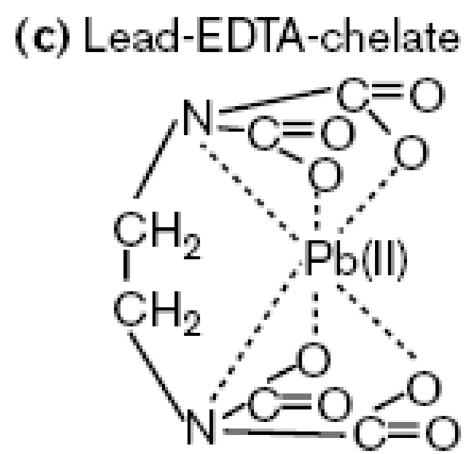
Active transporters are shown as boxes with arrows.

Plants experience oxidative stress upon exposure to heavy metals that leads to cellular damage. In addition, plants accumulate metal ions that disturb cellular ionic homeostasis. To minimize the detrimental effects of heavy metal exposure and their accumulation, plants have evolved detoxification mechanisms. Such mechanisms are mainly based on chelation and subcellular compartmentalization.

Among the heavy metal-binding ligands in plant cells the Phytochelatins (PCs) and Metallothioneins (MTs) are the best characterized. PCs and MTs are different classes of cysteine-rich, heavy metal-binding protein molecules.



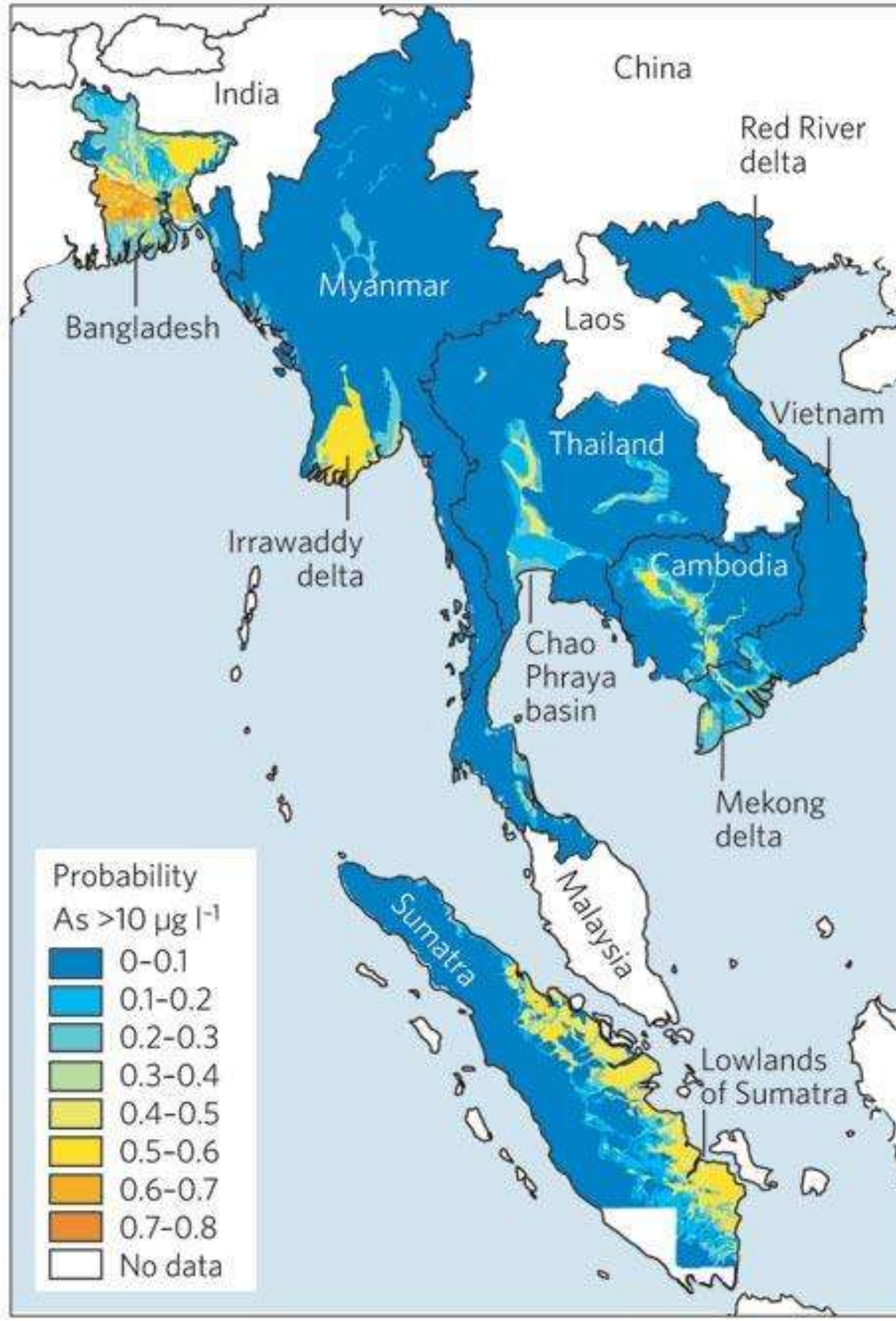




BIOACCUMULATION OF ARSENIC

In India and Bangladesh (around the Bay of Bengal) ~400 million people are at risk of arsenic poisoning, and up to 40 million people drink well water containing toxic levels of arsenic.

The problem affects most villages surrounding the river Ganga in both West Bengal and Bangladesh. Arsenic can be found in 63 of the 64 districts in Bangladesh.

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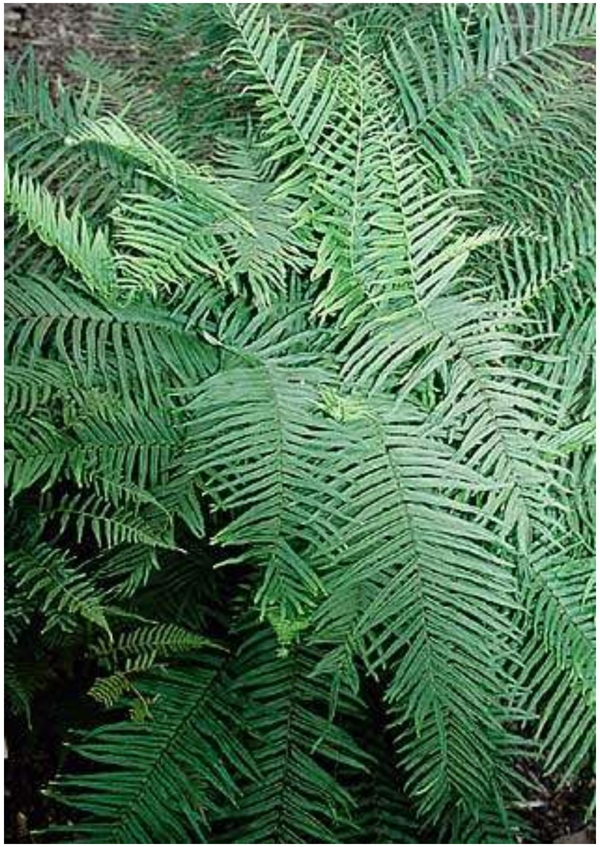
Phytoextraction of Arsenic by Chinese brake fern (*Pteris vittata* L.)



The Chinese Ladder fern *Pteris vittata*, also known as the brake fern, is a highly efficient accumulator of arsenic. *P. vittata* grows rapidly and can absorb up to 2% of its weight in arsenic.

In most plants, only a small fraction of the arsenic taken up from soil by roots accumulates in the above-ground tissue (<20%), whereas *P. vittata* accumulates up to 95% of the arsenic in above-ground tissue.

► For two growing cycles along with application of di-ammonium phosphate as a phosphatic fertilizer resulted in greater phyto-extraction of arsenic and improved the rice grain yields.

PHYTODEGRADATION OF EXPLOSIVES

Exposure to TNT and RDX, and their degradation products causes symptoms such as anemia and liver damage. These chemicals can be lethal and are suspected carcinogens.

Hundreds of tons of these compounds are found in sediments at innumerable manufacturing sites and storage sites for unexploded ordnance around the world. Tens of thousands of acres of land and water resources are unsafe because of RDX and TNT contamination.

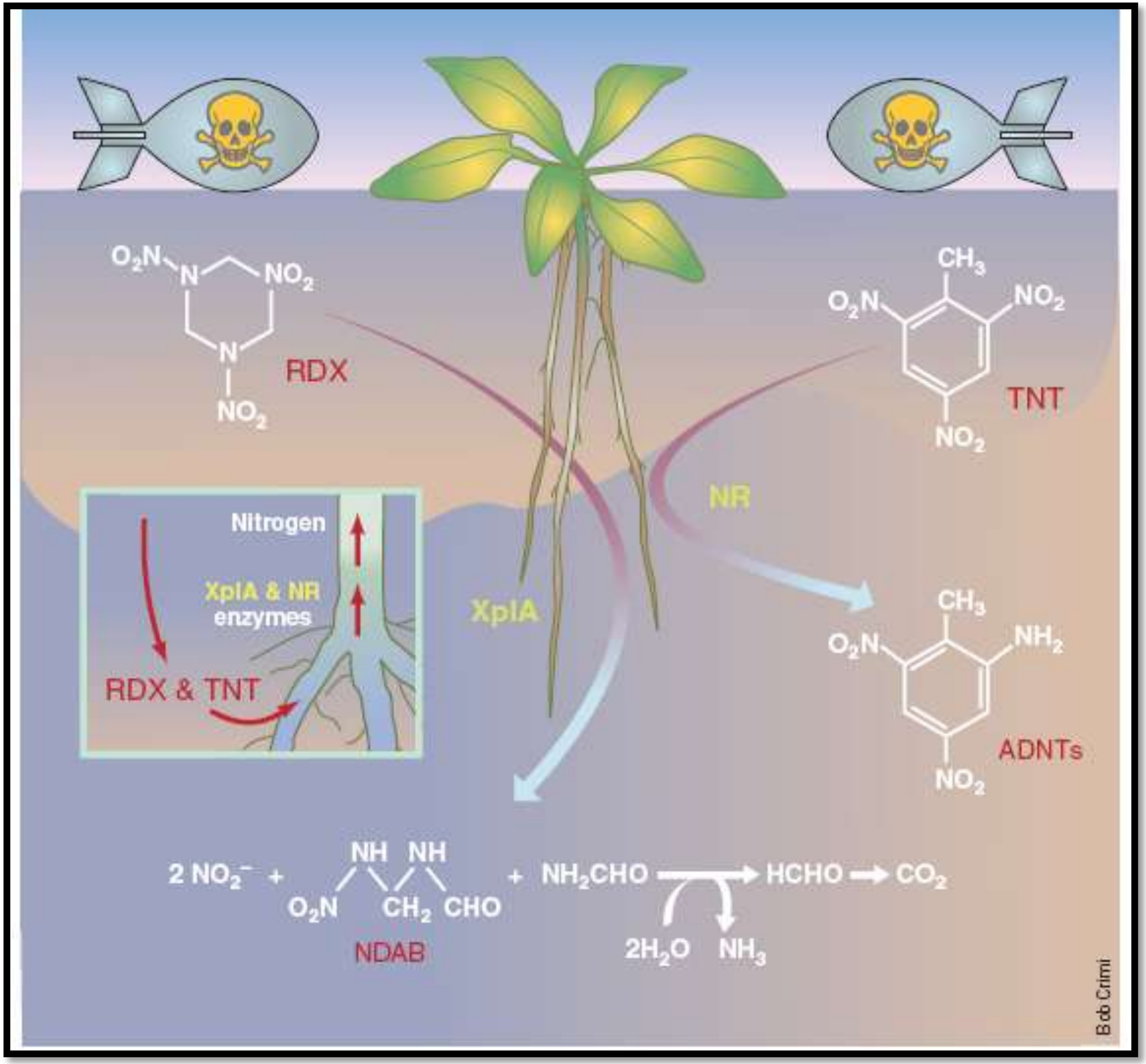
Arabidopsis Thaliana

NR:
Nitroreductase

XplA:
RDX-degrading
cytochrome P450

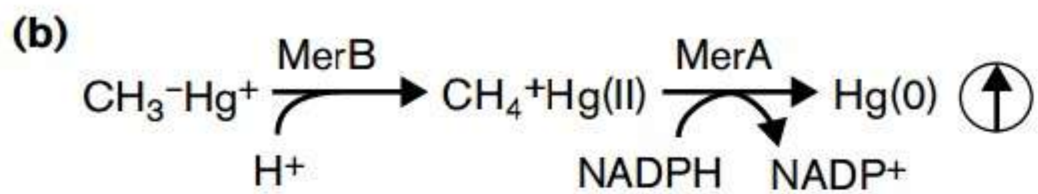
NDAB:
4-nitro-2,4-diazabutanal

ADNT:
Monoaminodinitrotoluene



THE ROLE OF GENETICS

Genetic engineering is a powerful method for enhancing natural phytoremediation capabilities, or for introducing new capabilities into plants Possibly, the most spectacular application of biotechnology for environmental restoration has been the bioengineering of plants capable of volatilizing mercury from soil contaminated with methyl-mercury.



Methyl-mercury, a strong neurotoxic agents, is biosynthesized in Hg contaminated soils. To detoxify this toxin, transgenic plants (***Arabidopsis* and tobacco**) were engineered to express bacterial genes *merB* and *merA*. In these modified plants, *merB* catalyzes the protonolysis of the carbon-mercury bond with the generation of Hg2+, a less mobile mercury species. Subsequently, *MerA* converts Hg(II) to Hg (0) a less toxic, volatile element which is released into the atmosphere .

CONCLUSION

• Phytoremediation is an emerging technology that employs the use of higher plants for the cleanup of contaminated environments.

• The main advantage of phytoextraction is environmental friendliness. Traditional methods which are used for cleaning up heavy metal contaminated soil disrupt soil structure and reduce soil productivity, whereas phytoextraction can clean up the soil without causing any kind of harm to soil quality.

• Another benefit of phytoextraction is that it is less expensive than any other clean up process and the possibility of the recovery and re-use of valuable metals .

• The possibility of using biotechnology to improve the efficiency of pytoremediation processes makes even better than any other existing methods.

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THANK YOU

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