Review

PHYTOREMEDIATION : GREEN TO CLEAN ENVIRONMENTAL HEAVY METAL POLLUTION

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Introduction

Many natural processes and anthropogenic activities lead to the persistent accumulation of non-biodegradable heavy metals in the environment. This contamination further has the potential to enter the food chain by a process called bioaccumulation and further, the concentration of heavy metal raises exponentially from lower to higher trophic levels as it is consumed called biomagnification. With the perspective of the consequences associated with heavy metal toxicity including risks to ecosystem and human health (mutagenic, carcinogenic, and teratogenic), the reclamation of toxic accumulates in soil and water is of paramount importance. Presently, clean-up technologies for heavy metals primarily concentrate on mitigating toxicity using physicochemical and mechanical methods such as soil incineration, excavation, landfilling, soil washing, solidification, and the application of electric fields. However, these are expensive, time-consuming, and also result in destructive changes to soil's physicochemical and biological properties, causing secondary pollution to the soil ecosystem. Therefore, the use of the inherent plant's ability to absorb ionic compounds even at low concentrations near the soil-root interface can be effectively employed as a strategy to extract and remove or lower the bioavailable toxic metals and this phenomenon is called phytoremediation.

Heavy metals and Global environmental issues

Ironically with the industrialization and disturbances in the biological cycle, heavy metal accumulation (e.g. $5.6\text{-}38 \times 10^6$ kg Cd/year) has become a substantial challenging issue of global concern. The most common routes of their entry into the environment are either weathering of rocks, erosion, and volcanic erosions as natural processes or mining, smelting, industrial effluent, and sludge, biosolids, pesticides, and manures as anthropogenic activities. As of now, fifty-three elements are classified as heavy metals and are regarded as universal pollutants based on densities greater than $5 g/cm^3 \neg$. They are further classified as essential and non-essential. Essential heavy metals, including Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), and Zinc (Zn) are vital for growth and development of plant; yet, at elevated levels, they turn out to be detrimental; and nonessential heavy metals Cadmium (Cd), Lead (Pb), Arsenic (As), and Mercury (Hg) do not have a described physiological role and pose potential toxicity, impacting both physiological and biochemical processes and thereby affecting crop yields. The organic

horizons of topsoil have a greater propensity to bind heavy metals and its concentration range between 1 to 1,00,000 mg/kg of soil. Crops grown in such soils mainly vegetables are prone to uptake heavy metals along with other essential elements near the soil-root interface and henceforth they are not advisable for human consumption.

As metals cannot be disintegrated, their accumulation in the organisms of successive trophic levels above the threshold leads to direct toxicity by cell structure damage due to reactive oxygen species-mediated oxidative stress and inhibition of various cytosolic enzymes. Furthermore, indirect toxic effects are caused due to the substitution of essential nutrients by heavy metals at basic metal ion exchange sites ultimately causing aberration in metabolic functions of cells and affecting growth and development cell death. In humans, depending on their oxidation state and concentration cause different health complications.

Heavy metals and their health complications

Heavy metal	Health consequence
As (Arsenic)	Analog of phosphate; inhibits ATP synthesis and oxidative phosphorylation
Cd (Cadmium)	Inhibits by calcium regulation causing renal failure and anemia
Cu (Copper)	Liver cirrhosis, brain, and kidney damage
Hg (Mercury)	Autoimmune diseases, fatigue, hair loss, ulcers, and brain damage
Pb (Lead)	Impaired development, short-term memory loss, renal failure in children
Zn (Zinc)	Fatigue and dizziness
Cr (Chromium)	Ulcers, respiratory problems, skin cancer, and hair loss
Ni (Nickel)	Dermatitis, lung cancer, sinus, and throat cancer

Strategies in option to mitigate heavy metal pollution

Reclamation of heavy metal pollution in soils is the prerequisite concern of environmental legislation and it can be carried out by in-situ and ex-situ approaches. In-situ decontamination is comparatively environmentally safe and economical than ex-situ methods and is based on principles of bioavailability following either complete removal or transformation of contaminants into harmless soil matter. Currently, certain conventional physicochemical methods like soil replacement, thermal desorption, and immobilization by chemical precipitation are employed for extensively affected heavy metal soils. However, the adoption of these strategies is constrained due to detrimental repercussions on soil structure and health consequently productivity. Therefore, the implementation of biological remediation methods including bioremediation by microorganisms and phytoremediation by plants is practically imperative and environmentally sustainable. Thereby reclaiming the polluted soil and stabilizing soil fertility.
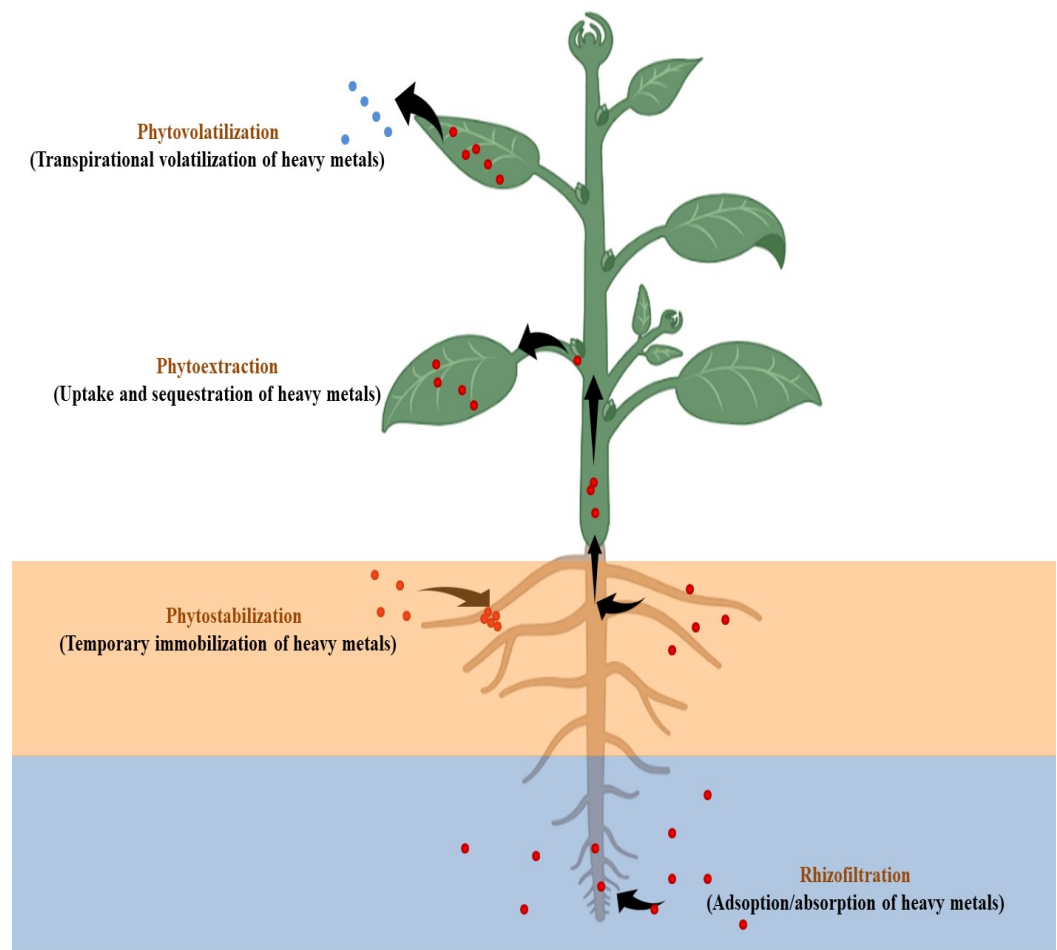
Figure 1: Phytoremediation strategies by plant

Phytostabilization: It employs metal-tolerant plants to temporarily immobilize heavy metals underground by reducing their bioavailability and thereby limiting their entry into the ecosystem. In this process, the rhizosphere can facilitate precipitation or reduction of metal valence. further, heavy metals can be absorbed and sequestered within root tissues or adsorbed onto the cell walls of the roots. Further, the addition of organic or inorganic amendments to contaminated soil enhance phytostabilization by altering metal speciation, heavy metal solubility, and bioavailability through changing soil pH and redox status.

Phytoextraction: It involves using plants to uptake and accumulate contaminants from soil or water in their aboveground biomass. In contrast to phytostabilization which temporarily confines heavy metals underground, phytoextraction offers a permanent remedy for eliminating heavy metals from contaminated soil. Effective phytoextraction relies on factors like plant selection, performance, metal bioavailability, and soil properties. Two strategies are used for plant selection: hyperaccumulators that accumulate high levels of metals in aboveground parts, and high biomass producers including Helianthus annuus, Cannabis sativa, Trifolium alexandrinum that compensate with overall accumulation. Further, non-edible hyperaccumulators are preferred to avoid heavy metal entry into the food chain.

Phytovolatilization: Here plants absorb soil pollutants from the rhizosphere and convert and release them into the atmosphere as less toxic volatile forms through transpiration. It effectively detoxifies organic pollutants and certain heavy metals like selenium (Se), mercury (Hg), and arsenic (As). *Brassica juncea* is known for its

ability to volatilize Se. Although phytovolatilization removes pollutants from the site without plant harvesting, it doesn't completely eliminate them. Pollutants are transferred to the atmosphere, potentially contaminating the air and being redeposited into the soil through precipitation. Risk assessment is crucial before implementing phytovolatilization.

Phytofiltration: is a phytoremediation method that utilizes seedlings (blastofiltration), shoots (caulofiltration), or plant roots (rhizofiltration) to withdraw pollutants from contaminated water. During rhizofiltration, root exudates secreted by plant roots aid the uptake/adsorption of heavy metals by/onto plant roots. These exudates play a crucial role in altering the pH of the rhizosphere, which promotes the precipitation of heavy metals onto the roots. Plants are initially grown hydroponically in clean water to develop a strong root system before being acclimated to the polluted water. Once acclimated, they are transferred to the contaminated site to remove heavy metals. Ideal plants for phytofiltration have dense root systems, high biomass production, and tolerance to heavy metals. Aquatic species such as azolla, cattail, duckweed, hyacinth, and poplar are commonly employed for wetland water remediation, while terrestrial plants such as Indian mustard and sunflower demonstrate good heavy metal accumulation capacity during rhizofiltration.

Interventions to enhance the phytoremediation abilities

Genetic engineering: a promising strategy involves transferring foreign genes from organisms such as plants, bacteria, or animals into the genome of target plants, conferring specific traits. Compared to traditional breeding, genetic engineering offers advantages of faster modification. Engineering fast-growing, high-biomass plants for increased heavy metal tolerance or accumulation is more practical than modifying hyperaccumulators. Strategies include enhancing antioxidant activity to improve heavy metal tolerance and introducing genes encoding metal transporters or chelators to enhance accumulation. However, challenges include the complexity of heavy metal detoxification and accumulation mechanisms, as well as regulatory hurdles due to safety concerns. Alternative approaches are needed when genetic engineering is impractical.

Microbes: Plant-associated microorganisms, such as plant growth-promoting rhizobacteria (PGPR) and arbuscular mycorrhizal fungi (AMF), enhance plant performance in phytoremediation. PGPR promotes plant growth, increases heavy metal tolerance, and improves nutrient and heavy metal uptake through the production of various compounds. They can also stimulate root development and produce bacterial auxin to facilitate phytoremediation. Further, the extensive hyphal network of AMF enhances water and nutrient uptake by increasing the root surface area for absorption. Additionally, they produce phytohormones that promote plant growth and aid in phytoremediation.

Metal chelation: Not all heavy metals in the soil except Zn and Cd are readily available for plant uptake, as they may exist in insoluble forms and partly depends on soil properties, such as pH, and their binding to soil particles. Plants can enhance bioavailability by secreting compounds that acidify the rhizosphere, promoting the release of heavy metals from complexes. Plant-associated microorganisms, such as PGPR and mycorrhizal fungi, can also increase bioavailability through the secretion of chelating agents and enzymes. Using chelating agents, both synthetic (ethylene diamine tetraacetic acid, ethylene glycol tetraacetic acid, etc) and organic (citric acid, malic acid, etc), can further improve heavy metal solubility and uptake, with organic chelators being more environmentally friendly.

Conclusion

Heavy metal pollution poses significant challenges to agriculture and food safety. Phytoremediation is a promising technique for revegetating contaminated soil, but it has limitations such as slow cleanup. Genetic engineering offers a powerful tool to enhance plant performance by improving traits like growth, biomass production, metal tolerance, and accumulation. Combining genetic engineering with microbe-assisted and chelate-assisted approaches will be crucial for effective phytoremediation.

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