

Phytoremediation Technologies for Heavy Metal Contaminated Soils

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Abstract

Soil contamination by heavy metals (e.g., Cd, Pb, Cr, As, Hg, Ni, Zn, Cu) poses a severe threat to global ecosystems, food security, and human health. Traditional physical and chemical remediation methods are often prohibitively expensive, destructive to soil ecology, and unsuitable for large-scale applications. Phytoremediation, the use of plants and their associated microbiota to stabilize, extract, degrade, or volatilize contaminants, has emerged as a promising, cost-effective, solar-driven, and ecologically sustainable alternative. This comprehensive review synthesizes the state-of-the-art in phytoremediation technologies specifically designed for heavy metal-contaminated soils. We detail the core mechanisms: phytoextraction (uptake and accumulation in harvestable biomass), phytostabilization (immobilization and reduction of bioavailability), phytovolatilization (conversion and release to the atmosphere), and phytodegradation/rhizodegradation (microbial degradation in the root zone). A critical analysis of hyperaccumulator species-their discovery, physiology, and genetic basis for metal tolerance and accumulation-is provided. The review further examines the pivotal role of soil amendments (chelators, biochar, fertilizers) and plant growth-promoting rhizobacteria (PGPR) in enhancing remediation efficiency. We evaluate the agronomic management practices for field-scale application and present a series of global case studies showcasing successful implementation. However, significant challenges remain, including slow remediation rates, biomass disposal, potential for food chain contamination, and climate dependencies. This article explores cutting-edge strategies to overcome these limitations, such as genetic engineering for enhanced metal uptake and tolerance, intercropping systems, and the integration of phytoremediation with bioenergy production (phytomining). Finally, we propose a multi-criteria framework for technology selection and outline future research directions aimed at optimizing phytoremediation for wider commercial and environmental adoption, positioning it as a cornerstone of the circular economy and sustainable land management.

Keywords

Phytoremediation, Heavy Metals, Hyperaccumulator, Phytoextraction, Phytostabilization, Soil Contamination, Plant Growth-Promoting Rhizobacteria, Chelate-Assisted Remediation, Genetic Engineering

1. Introduction

The Scale of the Problem and the Promise of Green Technology

Heavy metal contamination of soils is a pervasive and persistent environmental legacy of industrial activities, mining, improper waste disposal, agricultural chemical overuse, and urbanization [1]. Unlike organic pollutants, metals are non-biodegradable and can persist in soils for millennia, posing long-term risks. Their bioavailability allows entry into the food chain, leading to bioaccumulation and biomagnification, with profound toxic effects on flora, fauna, and humans, including neurological damage, cancer, and organ failure. The global extent of contaminated land is vast, demanding remediation solutions that are not only effective but also economically viable and environmentally benign [2].

Traditional ex-situ methods (e.g., excavation, soil washing, thermal treatment) and in-situ chemical treatments (e.g., solidification, vitrification) are often characterized by high costs, high energy consumption, secondary pollution, and severe disturbance to soil structure and biology [3]. These limitations have catalysed the search for "gentler" alternatives.

Phytoremediation represents a paradigm shift towards green and sustainable remediation. It harnesses the natural physiological and biochemical processes of plants, often in synergy with their root-associated microbes, to mitigate soil contamination. While slower than engineered solutions, its advantages are compelling: it is aesthetically pleasing, preserves topsoil fertility, promotes biodiversity, minimizes secondary waste, and offers potentially very low costs per treated area. Furthermore, it aligns with the principles of circular economy through possibilities like phytomining (recovery of valuable metals) and biomass valorization for bioenergy [4].

This review provides a systematic analysis of phytoremediation as a technology suite for heavy metals. We dissect its scientific foundations, evaluate its practical applications, confront its inherent challenges, and explore innovative strategies that are pushing the boundaries of this dynamic field.

2. Core Mechanisms of Phytoremediation for Heavy Metals

Phytoremediation is not a single process but a collection of distinct mechanisms, each suited to specific contaminants, soil conditions, and remediation goals. Understanding these is key to selecting and optimizing the technology.

2.1 Phytoextraction

Phytoextraction is the most prominent mechanism for metal removal. It involves the uptake of metals from the soil by plant roots, their translocation to above-ground shoots, and subsequent harvest and removal of the metal-rich biomass [5].

- Process:** Soluble metal ions are absorbed via root membranes (through transporters often intended for essential nutrients like Ca^{2+} , Fe^{2+} , or Zn^{2+}). Inside the plant, metals are chelated by ligands (e.g., phytochelatins, metallothioneins) and sequestered in vacuoles of leaf cells to minimize toxicity.

- Ideal Plants:** Hyperaccumulators—a unique group of ~500 plant species capable of accumulating metals at concentrations 100-1000 times greater than ordinary plants without suffering phytotoxicity. Examples include *Noccaea caerulea* (Zn, Cd, Ni), *Pteris vittata* (As), and *Sedum alfredii* (Cd, Zn).

- Goal:** Permanent removal of metals from the site.

2.2 Phytostabilization

Also known as phytosequestration, this approach aims not to remove metals but to immobilize them *in situ*, reducing their bioavailability, mobility, and risk of leaching into groundwater or entering the food chain.

- Process:** Plants stabilize metals through: (1) Precipitation in the rhizosphere via root exudates altering pH, (2) Adsorption and adsorption onto root surfaces or within root tissues, and (3) Complexation with exuded organic compounds.

- Ideal Plants:** Fast-growing, dense-rooted, tolerant species (often non-hyperaccumulators) that provide good soil cover, prevent erosion, and promote conditions for metal stabilization. Grasses, shrubs, and trees like willows (*Salix* spp.) and poplars (*Populus* spp.) are commonly used [6].

- Goal:** Risk management, erosion control, and site restoration.

2.3 Phytovolatilization

This process involves the uptake of metals, their bioconversion into volatile species within the plant, and subsequent release into the atmosphere through transpiration.

- Process:** Applicable mainly to metalloids like Selenium (Se) and Mercury (Hg). Plants metabolize inorganic Se (e.g., selenate) to dimethylselenide (DMSe), and inorganic Hg to elemental Hg(0), which are gases [7].

- Ideal Plants:** Species with high transpiration rates and the necessary enzymatic pathways (e.g., *Brassica juncea* for Se).

- Consideration:** Controversial because it transfers contamination from soil to air, albeit often in a less toxic form. Requires careful risk assessment.

2.4 Phytodegradation and Rhizodegradation

While more relevant for organic pollutants, microbial degradation in the root zone (rhizodegradation) can influence metal speciation and bioavailability. Plant exudates (sugars, acids, enzymes) stimulate microbial activity, which can alter metal redox states (e.g., Cr(VI) to Cr(III)) or degrade metal-organic complexes.

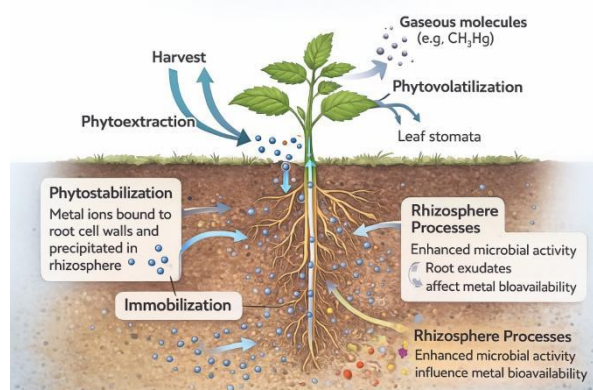


Figure 1. Schematic overview of key phytoremediation mechanisms for heavy metals.

Figure 1 provides a comprehensive overview of the four major mechanisms involved in phytoremediation—a plant-based strategy used to manage, transform, or remove heavy metals and pollutants from contaminated soils. By illustrating the

plant, its root system, and the surrounding soil environment in cross-section, the image emphasizes that phytoremediation is not a single process but a coordinated set of biological, chemical, and ecological interactions occurring both within the plant and in the rhizosphere.

2.4.1 Phytoextraction: Uptake and Translocation of Metals Into Aboveground Biomass

The first mechanism depicted is phytoextraction, where metal ions present in contaminated soil are absorbed by the plant's roots and transported upward through the xylem into stems and leaves. These metals accumulate in the aboveground biomass, which can later be removed through harvesting. This process gradually decreases the concentration of heavy metals in the soil.

Phytoextraction is particularly effective for metals such as cadmium, zinc, and nickel, especially when hyperaccumulator plant species are used. The diagram shows blue dots representing metal ions moving upward and the "Harvest" label indicating that biomass removal is essential to achieving soil cleanup. This mechanism is widely considered one of the most direct and environmentally friendly methods for decontaminating polluted soils.

2.4.2 Phytostabilization: Root-Mediated Immobilization of Toxic Metals

The second pathway illustrated is phytostabilization, where contaminants remain primarily in the root zone rather than entering the plant's vascular system. In this mechanism, metal ions become immobilized through adsorption onto root cell walls, complexation with organic compounds, or precipitation within the rhizosphere. The diagram labels this process as "Immobilization," emphasizing its goal: to reduce the mobility, leachability, and bioavailability of harmful metals.

Phytostabilization does not remove contaminants from the soil, but it significantly limits their spread through erosion, groundwater transport, or plant uptake by other organisms. It is especially valuable for stabilizing metals such as lead and chromium, which are difficult for plants to extract. As a long-term management strategy, phytostabilization promotes soil stabilization while supporting gradual ecological recovery.

2.4.3 Phytovolatilization: Transformation and Release of Contaminants as Gas

The third process shown is phytovolatilization, where certain pollutants absorbed by plants are chemically transformed into volatile, often less toxic, gaseous compounds and released through stomata on the leaves. The diagram indicates this through upward arrows and gaseous molecules (e.g., CH_3Hg).

Although this mechanism does not remove pollutants from the environment, it converts them into gaseous forms that disperse in the atmosphere at low concentrations. This process is commonly associated with elements such as mercury and selenium. The ecological implications of phytovolatilization are still debated, but when properly managed, it can be an efficient method for reducing soil concentrations of specific toxic metals.

2.4.4 Rhizosphere Processes: Microbial Interactions that Modify Metal Bioavailability

The final mechanism illustrated involves rhizosphere processes, which highlight the critical role of soil microorganisms and root exudates in shaping the chemical environment around plant roots. The diagram shows microbial activity enhanced by compounds released by roots, such as organic acids, amino acids, and enzymes.

These exudates can alter soil pH, redox potential, and chemical equilibria, thereby changing the solubility and mobility of metals. Microbial communities further contribute by transforming metals through reduction, oxidation, methylation, or immobilization. This collaborative plant-microbe interaction determines whether contaminants are more readily absorbed, immobilized, or degraded.

Thus, rhizosphere processes serve as a regulatory layer that enhances the efficiency of all other phytoremediation mechanisms.

Overall, the figure demonstrates that phytoremediation is a multifaceted process combining plant physiology, soil chemistry, and microbial ecology. Rather than functioning independently, these mechanisms reinforce one another to manage contaminants. Phytoextraction removes pollutants from soil, phytostabilization prevents further spread, phytovolatilization transforms certain contaminants into gaseous forms, and rhizosphere processes act as the biochemical engine that determines the rate and extent of each pathway. Together, they form an adaptable, low-cost, and environmentally sustainable approach to soil restoration.

3. The Hyperaccumulator Phenomenon: Physiology and Genetics

Hyperaccumulators are the workhorses of efficient phytoextraction. Their unique biology is key to advancing the technology [8].

3.1 Defining Traits and Physiological Adaptations

A hyperaccumulator typically has a shoot-to-root metal concentration ratio >1 and an absolute shoot concentration exceeding a defined threshold (e.g., $>100 \mu\text{g/g}$ for Cd, $>1000 \mu\text{g/g}$ for Ni, Cu, Co, Pb). Their adaptations involve:

- Enhanced Uptake:** Overexpression or altered regulation of metal transporter proteins (e.g., ZIP, NRAMP, HMA families) in root cells [9].
- Efficient Translocation:** Effective loading of metal-ligand complexes into the xylem sap for transport to shoots, often involving specific transporters like HMA4 [10].
- Detoxification & Sequestration:** Robust synthesis of metal-chelating molecules (phytochelatins, organic acids) and compartmentalization in leaf vacuoles or trichomes, isolating the metal from sensitive metabolic sites.
- Oxidative Stress Tolerance:** Enhanced antioxidant systems (superoxide dismutase, catalase, glutathione) to cope with metal-induced reactive oxygen species (ROS).

Table 1. Selected hyperaccumulator plants and their target metals.

Plant Species	Common Name	Target Heavy Metal(s)	Typical Accumulation (mg/kg dry weight)	Notable Region/Application
<i>Nocca caerulea</i> (formerly <i>Thlaspi caerulea</i>)	Alpine Pennycress	Zn, Cd, Ni	Zn: 30,000; Cd: 1,500	Europe; model species for Zn/Cd
<i>Pteris vittata</i>	Chinese Brake Fern	Arsenic (As)	As: 5,000 - 22,000	Global; first discovered As hyperaccumulator
<i>Sedum alfredii</i>	-	Cd, Zn	Cd: 5,000; Zn: 20,000	China; Cd hyperaccumulation in Crassulaceae
<i>Alyssum bertolonii</i>	-	Nickel (Ni)	Ni: 13,000	Mediterranean serpentine soils
<i>Elsholtzia splendens</i>	-	Copper (Cu)	Cu: 10,000	China; Cu mine tailings
<i>Helianthus annuus</i>	Sunflower	Pb, Cs, U (moderate)	Pb: 5,000+ (with chelates)	Widely used in assisted phytoextraction

Table 1 summarizes several well-known hyperaccumulator plant species and the specific heavy metals that they are capable of accumulating at exceptionally high concentrations in their tissues. Hyperaccumulator plants are a rare group-representing less than 0.2% of all vascular plants-that can tolerate, uptake, and store unusually large amounts of toxic metals without experiencing physiological damage. Because of these characteristics, they are of great interest in environmental remediation, especially for phytoremediation, phytomining, and the restoration of contaminated sites such as mining areas, industrial regions, and polluted soils.

3.2 Genetic Basis and the Potential of 'Omics'

Modern genomic, transcriptomic, and proteomic studies are unraveling the molecular networks behind hyperaccumulation. Identifying key genes (e.g., *HMA4*, *PCS1*, *IRT1*) opens avenues for **genetic engineering** to transfer these traits into high-biomass, agronomically suited plants, a strategy known as developing "super-phytoremediators."

4. Enhancing Phytoremediation Efficiency: Agronomic and Chemical Strategies

Natural hyperaccumulation is often slow for field remediation. Several enhancement strategies are employed:

4.1 Chelate-Assisted Phytoextraction

This involves adding synthetic (e.g., EDTA, EDDS) or natural (e.g., citric acid, oxalic acid) chelating agents to the soil. They solubilize bound metals, forming metal-chelate complexes that are more readily taken up by plants (including non-hyperaccumulators with high biomass). Caution: Must be managed carefully to prevent groundwater leaching of mobilized metals [11].

4.2 Soil Amendment with Biochar and Other Agents

Biochar, a carbon-rich porous material produced from biomass pyrolysis, is highly effective. It can:

- Immobilize Metals:** Via adsorption, cation exchange, and complexation, making it ideal for phytostabilization.
- Improve Soil Health:** Enhance water-holding capacity, nutrient retention, and microbial activity, supporting plant growth on degraded soils [12].
- Other amendments** include lime (to raise pH and immobilize many metals), organic compost (to improve soil structure and bind metals), and phosphate compounds (to precipitate Pb as pyromorphite).

4.3 Microbial-Assisted Phytoremediation

Plant Growth-Promoting Rhizobacteria (PGPR) and metal-tolerant fungi (including mycorrhizae) play a crucial role. They can:

- Promote Growth:** By producing phytohormones, fixing nitrogen, and solubilizing phosphates in stressed soils [13].
- Facilitate Uptake:** Alter rhizosphere pH, secrete siderophores and biosurfactants, and increase root surface area (mycorrhizae), enhancing metal bioavailability for uptake.

- Detoxify: Some bacteria can transform metals into less toxic forms via redox reactions or methylation.

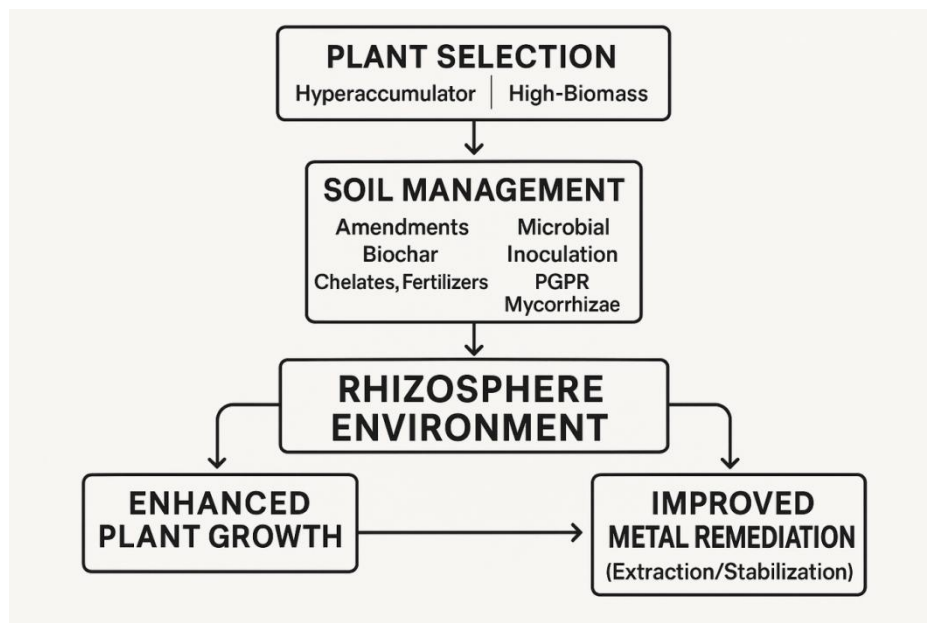


Figure 2. Integrated strategies for enhanced phytoremediation efficiency.

Figure 2 shows a flowchart how different management choices interact to enhance phytoremediation efficiency. It begins with plant selection, where the practitioner chooses either *hyperaccumulator* species, which take up high concentrations of metals, or *high-biomass* species, which produce large amounts of plant material. This choice then informs soil management strategies. Amendments such as biochar, chelating agents, and fertilizers are added to modify pH, nutrient status, and metal availability, while microbial inoculation with PGPR (plant growth-promoting rhizobacteria) and mycorrhizal fungi improves nutrient uptake and root health. Together, these inputs optimize the rhizosphere environment, the narrow zone of soil surrounding plant roots where intense biological and chemical interactions occur. A well-managed rhizosphere supports enhanced plant growth, increasing root surface area and above-ground biomass. At the same time, it promotes improved metal remediation, either by increasing metal extraction into plant tissues or by stabilizing metals in less mobile and less bioavailable forms. Overall, the diagram emphasizes that successful phytoremediation depends on the integrated design of plant choice and soil-microbe management rather than on any single factor alone.

5. From Laboratory to Field: Implementation and Case Studies

Successful field application requires careful planning and management.

5.1 Site Assessment and Technology Selection

A preliminary site characterization (metal types, concentrations, speciation, soil pH, texture, climate) is essential to choose between phytoextraction, phytostabilization, or a combined approach [14].

5.2 Agronomic Practices

- Crop Rotation/Intercropping: Using deep and shallow-rooted plants or metal-specific accumulators in sequence or combination to treat heterogeneous contamination [15].
- Irrigation and Fertilization: Optimal nutrient and water management is critical to maximize plant biomass, the "sink" for metals.
- Harvesting and Biomass Management: Timing of harvest to maximize metal yield. Biomass disposal options include composting (volume reduction), controlled incineration (ash as ore for phytomining), or anaerobic digestion for bioenergy [16].

5.3 Global Case Studies

- China: Large-scale use of *Sedum alfredii* for Cd remediation in agricultural soils of Zhejiang province.
- Europe: Field trials with *Noccaea caerulea* and *Salix* spp. for treating Cd/Zn-contaminated sites in Belgium and France.
- USA: Use of *Pteris vittata* for arsenic remediation at former pesticide and pressure-treated wood sites.
- Australia: Phytostabilization of gold mine tailings using native, metal-tolerant grasses and shrubs.

6. Challenges, Limitations, and Innovative Solutions

Despite its promise, phytoremediation faces significant hurdles:

1. Time-Intensive: Often requires multiple growing seasons (years to decades) for significant cleanup.
2. Depth Limitation: Effective only within the root zone (typically top 0.5-1 m of soil).
3. Biomass Disposal/Toxicity: Handling and processing contaminated biomass poses logistical and potential environmental risks.
4. Climate and Seasonality: Plant growth and remediation efficiency are halted in winter or dry seasons.
5. Potential for Food Chain Contamination: Risk of metal transfer if non-target organisms consume plant tissues.

Innovative Research Frontiers:

- Genetic Engineering: Creating transgenic plants with stacked traits: high biomass, deep roots, enhanced metal transport, and superior detoxification (e.g., overexpressing mercuric reductase for Hg phytovolatilization) [17].
- Phytomining: Cultivating hyperaccumulators on low-grade ores or contaminated land to commercially recover high-value metals like Ni, Au, Tl. This transforms remediation into a potential revenue stream [18].
- Integrated Remediation Concepts: Combining phytoremediation with other gentle technologies (e.g., electrokinetics to mobilize metals towards root zones) or using the biomass in constructed wetlands for treating metal-laden leachate.

7. Conclusion and Future Perspectives

Phytoremediation has matured from a conceptual curiosity to a viable component of the environmental remediation toolkit. Its strongest suit lies in the treatment of large, low-to-medium contaminated areas where gentle, *in-situ* management is prioritized over rapid, disruptive cleanup. The future of the field is interdisciplinary, integrating plant physiology, soil chemistry, microbiology, genetics, and agricultural engineering.

Key future directions include:

1. Precision Phytoremediation: Using sensors and modeling to dynamically manage amendments and irrigation.
2. Development of Commercial "Designer" Plants: Through both conventional breeding and genetic engineering, tailored for specific metal cocktails and climatic conditions.
3. Strengthening the Circular Economy Link: Optimizing valorization pathways for contaminated biomass, ensuring the technology is not only clean but also resource-efficient.
4. Policy and Acceptance: Developing clear regulatory frameworks for biomass disposal and encouraging market-based mechanisms (e.g., ecosystem service credits) to promote wider adoption.

In conclusion, phytoremediation offers a powerful, nature-based solution to one of industrialization's most stubborn legacies. By deepening our understanding and innovating its application, we can harness the humble plant's power to restore the health of our contaminated lands sustainably and effectively.

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