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Engineering Phytoremediation Frontiers: Comparative Performance of Sunflower and Other Plant Species under Nanoparticle-Assisted Strategies

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ABSTRACT

The global escalation of heavy metal pollution in soils, largely attributed to unregulated industrial expansion and unsustainable agricultural practices, necessitates environmentally sustainable and scalable remediation strategies. Phytoremediation the use of plants to extract, stabilize, or transform contaminants has emerged as a promising green technology due to its cost-effectiveness, ecological compatibility, and potential for long-term application. *Helianthus annuus* (sunflower) has gained attention for its high biomass production, broad-spectrum uptake of metals such as lead, cadmium, and zinc, and exceptional resilience under abiotic stress. This review provides a comparative assessment of the phytoremediation potential of *H. annuus* alongside other key species, including *Brassica juncea*, *Zea mays*, and *Sorghum bicolor*, across varied ecological and contamination scenarios. Furthermore, we explore the role of engineered nanomaterials—specifically zinc oxide (ZnO), iron oxide (Fe_3O_4), and titanium dioxide (TiO_2) nanoparticles—in enhancing metal bioavailability, modulating oxidative stress responses, and risks including nanoparticle-induced ecotoxicity and microbiome shifts. Finally, we identify emerging frontiers in precision-guided phytoremediation, facilitated by nanobiotechnology and bioinformatics, which promise to enhance selectivity, scalability, and environmental safety. This synthesis positions nanoparticle-assisted phytoremediation as a next-generation strategy for restoring metal-contaminated soils in alignment with sustainable development objectives.

Keywords: Phytoremediation, *Helianthus annuus* (Sunflower), Nanoparticles, Heavy Metal Pollution

1. INTRODUCTION

1.1 Heavy Metal Contamination: A Persistent Environmental Challenge

Soil contamination by heavy metals is increasingly recognized as a global environmental and public health crisis. This form of pollution stems primarily from anthropogenic activities such as mining, industrial effluent discharge, wastewater irrigation, and the excessive application of fertilizers and pesticides. As a result, toxic metals including cadmium (Cd), lead (Pb), zinc (Zn), copper (Cu), and nickel (Ni) are now prevalent in agricultural soils worldwide (Alengebawy et al., 2021; Tong et al., 2020). Unlike organic pollutants, these metals are non-biodegradable and persist in the environment for extended periods, where they accumulate in food chains and compromise soil health and ecosystem services (Rizvi et al., 2020; Sun et al., 2018). At the physiological level, heavy metal exposure induces oxidative stress, impairs photosynthesis, alters nutrient uptake, and disrupts cellular homeostasis in plants (Saidi et al., 2014; Alonso-Blázquez et al., 2015). In humans, dietary exposure through contaminated crops has been linked to neurotoxicity, nephrotoxicity, skeletal disorders, and carcinogenicity (Alengebawy et al., 2021), underscoring the urgent need for effective remediation technologies.

1.2 Phytoremediation: A Green Remediation Paradigm

Phytoremediation, the use of living plants to remediate contaminated environments, offers a low-cost and sustainable solution. It encompasses several mechanisms—phytoextraction, phytostabilization, phytodegradation, and rhizofiltration—depending on the contaminant profile and the plant species involved (Cecchin et al., 2017; Radziemska et al., 2017). Phytoremediation aligns with global sustainability goals by minimizing ecological disruption while restoring soil functionality (Fulekar, 2016; Prasad, 2007). However, its large-scale application remains constrained by factors such as limited biomass productivity, metal-specific uptake variability, and poor bioavailability of heavy metals in soil matrices. Recent innovations, including soil amendments, microbial symbioses, and nanotechnology, have emerged as potential solutions to enhance phytoremediation efficiency (Rizwan et al., 2019; Marques et al., 2013).

1.3 Sunflower (*Helianthus annuus*): A Model Phytoremediator

Among candidate species, *Helianthus annuus* (sunflower) has attracted considerable attention due to its rapid growth, extensive root system, high biomass yield, and tolerance to multiple heavy metals (Prasad, 2007; Angelova et al., 2016). It is particularly effective in accumulating metals such as Pb, Cd, Zn, Cu, and Ni across a range of soil conditions (Chhotu & Fulekar, 2008; Alaboudi et al., 2018; Francis, 2017). Comparative studies have consistently shown sunflower to outperform species like *Zea mays*, *Sorghum bicolor*, and *Brassica juncea* in metal uptake per unit area and shoot bioaccumulation (Hamvumba et al., 2014; Rahman et al., 2013). Additionally, the post-harvest biomass of sunflower can be valorized for bioenergy or material applications, providing both ecological and economic co-benefits (Dhiman et al., 2017).

1.4 Rationale for Comparative Review

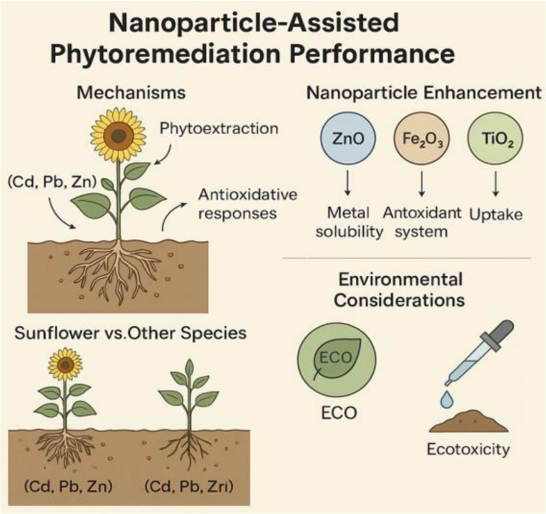
While individual studies on plant-assisted and nanoparticle-assisted remediation abound, comprehensive comparative assessments across plant species and nanoparticle types remain limited. Despite the growing body of literature supporting sunflower's phytoremediation efficiency, few studies provide head-to-head comparisons with other widely used species using standardized metrics. Such cross-species analyses are critical for guiding policy, plant selection, and field deployment strategies in nanotechnology-assisted remediation.

2. MECHANISMS OF HEAVY METAL UPTAKE AND DETOXIFICATION IN PLANTS

A mechanistic understanding of how plants perceive, absorb, translocate, and detoxify heavy metals is central to enhancing phytoremediation efficiency. These physiological, biochemical, and molecular processes determine not only the plant's capacity to accumulate metals but also its ability to mitigate toxicity while sustaining growth and productivity.

2.1 Root Uptake and Transport Systems

Heavy metal uptake is initiated at the root–soil interface, where metals enter plant tissues either passively via apoplastic diffusion or actively through selective membrane transporters. Active uptake is particularly crucial under low metal concentrations or when competition among metal ions occurs in the rhizosphere.Key transporter families mediate metal ion acquisition. The ZRT-IRT-like Protein (ZIP) family facilitates the uptake of divalent metal cations, including Zn^{2+}, Fe^{2+}, Mn^{2+}, and Cd^{2+}, across the plasma membrane (Barabasz et al., 2019; Tiong et al., 2014). The Natural Resistance-Associated Macrophage Protein (NRAMP) family, widely expressed under metal deficiency, contributes to the uptake and intracellular mobilization of Fe, Mn, and Cd. Furthermore, Heavy Metal ATPases (HMAs)—particularly the P1B-type subclass—are involved in metal efflux, vacuolar sequestration, and xylem loading of Zn, Cd, and Pb (Rivelli et al., 2012). These transporters are often upregulated in metal-contaminated soils, making them valuable molecular biomarkers for plant metal stress response.



2.2 Translocation and Redistribution

Following uptake, metals must be translocated to aerial tissues to enable phytoextraction. This redistribution is facilitated by chelation with organic ligands, including histidine, nicotianamine, and phytochelatins, which not only enhance solubility but also buffer the toxic effects of free metal ions (Barabasz et al., 2019). These metal–ligand complexes are loaded into the xylem and transported to shoots through the coordinated action of HMAs and metallochaperones. In hyperaccumulator species such as *Helianthus annuus*, this process is highly efficient, resulting in high shoot-to-root metal concentration ratios (Angelova et al., 2016; Francis, 2017). This characteristic is particularly advantageous in phytoremediation, as metals accumulated in harvestable tissues can be effectively removed from the system.

2.3 Oxidative Stress Response and Antioxidant Defense

Heavy metals frequently induce oxidative stress by generating reactive oxygen species (ROS), including superoxide radicals (O_2^-), hydrogen peroxide (H_2O_2), and hydroxyl radicals (•OH). These ROS damage lipids, proteins, and nucleic acids, ultimately impairing cellular functions (Saidi et al., 2014; Alonso-Blázquez et al., 2015). To counteract this, plants activate a robust antioxidant defense system comprising both enzymatic and non-enzymatic components. Among enzymatic antioxidants, superoxide dismutase (SOD) catalyzes the dismutation of O_2^- to H_2O_2, which is subsequently detoxified by catalase (CAT) and ascorbate peroxidase (APX). Glutathione reductase (GR) contributes to maintaining the redox balance via regeneration of reduced glutathione. In sunflower, significant upregulation of SOD and APX activity has been observed under Zn, Pb, and Cd stress, particularly when co-treated with nanoparticles (Rajiv et al., 2018; Hussain et al., 2018). Non-enzymatic antioxidants such as ascorbic acid, glutathione, flavonoids, and carotenoids work synergistically with enzymes to neutralize ROS. This multifaceted antioxidant network underpins the plant's resilience against metal-induced oxidative damage.

2.4 Role of Rhizospheric Microbes

The rhizosphere represents a dynamic interface where microbial communities profoundly influence metal availability and plant tolerance. Plant Growth-Promoting Rhizobacteria (PGPR) enhance phytoremediation via multiple mechanisms, including metal solubilization, production of phytohormones like indole-3-acetic acid (IAA), release of siderophores that chelate metals, and secretion of 1-aminocyclopropane-1-carboxylate (ACC) deaminase to alleviate ethylene-mediated stress. Inoculation of sunflower with PGPR has been shown to significantly enhance uptake of Cd and Zn while promoting biomass production under metal stress (Marques et al., 2013). When combined with nanoparticles or chelating agents such as EDTA, these microbial consortia can further amplify metal solubility and plant uptake, without compromising rhizosphere health (Turgut et al., 2004; Mahdieh et al., 2018).

2.5 Soil Physicochemical Factors

Soil characteristics play a pivotal role in determining metal mobility, bioavailability, and eventual plant uptake. Soil pH is particularly influential, with lower pH increasing the solubility of most heavy metals. Organic matter content affects metal complexation and microbial activity, while high cation exchange capacity (CEC) enhances metal retention. Soil texture also modulates mobility, with sandy soils favoring leaching and clayey soils retaining metals. Feizi et al. (2018) demonstrated that amending light-textured soils with modified clays and nanoparticles can strategically alter metal partitioning, thereby improving remediation outcomes.

3. PHYTOREMEDIATION POTENTIALS OF OTHER MAJOR SPECIES: A COMPARATIVE FRAMEWORK

While *Helianthus annuus* has emerged as a benchmark phytoremediator, several other plant species exhibit promising attributes across varied contamination profiles and agroecological zones. These include *Brassica juncea*, *Zea mays*, *Sorghum bicolor*, *Amaranthus paniculatus*, and *Vetiveria zizanioides*. This section offers a comparative assessment of these species, evaluating their metal specificity, biomass productivity, translocation efficiency, and compatibility with nanoparticle-assisted phytoremediation (NAPR) approaches.

3.1 Indian Mustard (*Brassica juncea*)

Brassica juncea is extensively studied for its phytoremediation capabilities due to its rapid life cycle, high root-to-shoot metal translocation, and strong biochemical detoxification pathways. It effectively accumulates cadmium (Cd), lead (Pb), zinc (Zn), nickel (Ni), and chromium (Cr), facilitated by its elevated synthesis of glutathione and phytochelatins (Rahman et al., 2013). Comparative studies have reported Pb uptake comparable to sunflower; however, its lower biomass limits total metal removal per harvest (Tariq & Ashraf, 2016). Nanoparticle co-application, particularly with ZnO in combination with EDTA, significantly enhances Cd and Ni uptake (Tripathi et al., 2017). Despite these advantages, *B. juncea* exhibits lower tolerance under high metal stress and tends to exhibit premature senescence, limiting its performance under extreme contamination.

3.2 Sorghum (*Sorghum bicolor*)

Sorghum bicolor is a drought-tolerant species known for its role in phytostabilization rather than extraction. It accumulates Pb, Cd, and arsenic (As), particularly in root tissues, suggesting its primary role in limiting metal mobility rather than harvesting contaminants (Hamvumba et al., 2014). In direct comparison to sunflower, sorghum displays lower translocation efficiency but higher retention in roots. Preliminary studies have indicated that TiO_2 nanoparticles and biochar amendments can stimulate antioxidant activity and improve root development (Lacalle et al., 2018), though comprehensive NAPR assessments remain limited. Its modest biomass also restricts its potential in large-scale remediation unless targeting shallow soil stabilization.

3.3 Amaranth (*Amaranthus paniculatus*)

Amaranthus paniculatus has demonstrated considerable potential for Cu, Pb, and Ni uptake through efficient chelation and vacuolar sequestration mechanisms. It outperformed *B. juncea* in Cu accumulation in certain experimental setups, despite producing lower biomass (Rahman et al., 2013). Its metal hyperaccumulation traits make it an intriguing candidate for further study, particularly in multi-metal systems. However, NAPR applications in amaranth remain virtually unexplored. Its rapid growth and adaptability suggest strong potential, warranting high-throughput phenotypic and nanoparticle compatibility evaluations.

3.4 Vetiver (*Vetiveria zizanioides*)

Vetiveria zizanioides is distinguished by its deep root system and remarkable tolerance to metal stress and degraded soils, particularly in post-mining environments. It efficiently stabilizes Pb, Cr, Ni, and Zn in the rhizosphere, making it ideal for erosion control and phytostabilization (Lacalle et al., 2018). While its shoot accumulation is modest compared to sunflower, its performance on marginal lands and compatibility with biochar and zero-valent iron nanoparticles offer strong practical advantages. It is particularly suited for non-harvest applications such as slope stabilization and tailing containment.

3.5 Future Research Opportunities

To advance the field, future research should prioritize high-throughput screening of underexplored species like *Amaranthus* under nanoparticle-assisted conditions. Integration of transcriptomic and ionomic profiling could elucidate species-specific pathways of uptake, detoxification, and oxidative response. Field-scale experiments involving multi-species comparisons under realistic contamination gradients are also crucial. Additionally, the development of eco-safe, plant-specific nanoparticle formulations tailored to different soil textures and crop systems will be key to optimizing performance while minimizing environmental risks.

Table: 2: **Comparative Table: Summary of Key Traits**

Species	**Target Metals**	**Biomass Yield**	**Translocation Factor**	**NAPR Compatibility**	**Best Application**
Helianthus annuus	Cd, Pb, Zn, Cu	High	High	Strong (ZnO, Fe_3O_4)	Phytoextraction
Brassica juncea	Cd, Pb, Cr	Medium	High	Moderate	Phytoextraction
Zea mays	Zn, Cu, Pb	High	Moderate	Strong	Dual use (food + cleanup)
Sorghum bicolor	Pb, Cd, As	Medium	Low	Moderate	Phytostabilization
Amaranthus paniculatus	Cu, Pb, Ni	Low	High	Unknown	Phytoextraction
Vetiveria zizanioides	Pb, Ni, Cr, Zn	Medium	Low	Limited	Phytostabilization

4. NANOPARTICLE-ASSISTED PHYTOREMEDIATION (NAPR): MECHANISMS, ENHANCEMENTS, AND CONCERNS

Nanotechnology has ushered in a transformative era in environmental remediation, offering tools to address longstanding limitations in conventional phytoremediation systems. Termed nanoparticle-assisted phytoremediation (NAPR), this emerging approach involves the strategic application of engineered nanomaterials to improve metal bioavailability, enhance plant physiological resilience, and modulate rhizosphere conditions. This section critically examines the mechanisms underlying NAPR, evaluates the performance of different nanoparticle classes, and discusses associated environmental and regulatory challenges.

4.1 Nanoparticles in Environmental Remediation: An Overview

Engineered nanoparticles (NPs), typically defined as particles with at least one dimension below 100 nm, possess high surface area-to-volume ratios, customizable surface chemistries, and enhanced reactivity. These properties allow NPs to participate in various soil and plant processes relevant to metal mobilization and detoxification. NPs can enhance phytoremediation by solubilizing or immobilizing toxic metals in soil matrices, interacting with root exudates to promote uptake, influencing microbial dynamics in the rhizosphere, and acting as carriers for nutrients or chelators (Feizi et al., 2018; Rizwan et al., 2021). In doing so, they alleviate phytotoxicity, support plant growth under stress, and improve phytoextraction outcomes.

4.2 Classes of Nanoparticles Used in Phytoremediation

4.2.1 Zinc Oxide (ZnO) Nanoparticles

ZnO NPs are widely studied due to their role as both micronutrients and modulators of metal mobility. Upon soil application, ZnO particles release Zn^{2+} ions that stimulate enzyme activity, metal transporter expression, and antioxidant defenses (Hussain et al., 2018). In *Helianthus annuus*, wheat, and rice, foliar and soil-applied ZnO NPs have significantly improved uptake of Cd, Pb, and Zn (Rajiv et al., 2018; Bashir et al., 2018). Additionally, ZnO is relatively biodegradable under UV light and exhibits low ecotoxicity at environmentally relevant concentrations, making it one of the more eco-compatible nanomaterials in this domain.

4.2.2 Iron Oxide (Fe_3O_4) Nanoparticles

Magnetite (Fe_3O_4) nanoparticles serve dual roles in plant stimulation and soil remediation. These NPs influence soil redox potential and organic matter interactions, thus enhancing trace metal solubility and bioavailability (He et al., 2017). Their magnetic properties allow for targeted soil applications and post-remediation retrieval. When combined with biochar or photosynthetic bacteria, Fe_3O_4 NPs have been shown to increase Pb and Cr uptake in *Zea mays* and sunflower, while simultaneously improving soil enzymatic activity and microbial viability (Lacalle et al., 2018).

4.2.3 Titanium Dioxide (TiO_2) Nanoparticles

TiO_2 NPs, known for their photocatalytic properties, enhance light absorption and photosynthetic efficiency in stressed plants. Their presence has been linked to increased chlorophyll synthesis, upregulation of antioxidant enzymes, and enhanced biomass accumulation under heavy metal stress (Kolenčík et al., 2020). In sunflower and barley, TiO_2 NPs have been reported to increase Zn and Cu uptake, while improving drought tolerance and stress signaling.

4.2.4 Carbon-Based Nanomaterials

Carbon-derived nanomaterials—including biochar nanoparticles, graphene oxide, and carbon nanotubes—offer multifaceted remediation benefits. Biochar NPs, in particular, act as metal adsorbents, improve soil aeration, and foster beneficial microbial communities (Seleiman et al., 2020). When applied alongside plant growth-promoting rhizobacteria (PGPR) or mycorrhizae, these nanomaterials enhance metal solubilization and uptake while buffering against abiotic stressors. Their large surface area and porous structure also support water retention and nutrient exchange, crucial for plant resilience in contaminated soils.

4.3 Regulatory Landscape and Future Prospects

The regulatory governance of nanoparticle use in environmental applications remains fragmented and underdeveloped. There is currently no globally harmonized framework for assessing the risks and benefits of nanomaterials in phytoremediation. Key challenges include the absence of standardized toxicity thresholds, inconsistent definitions of nanomaterials across jurisdictions, and a paucity of long-term ecotoxicological data (Ibrahim et al., 2016). To advance safe and scalable implementation of NAPR, several strategies are recommended. First, the eco-design of biodegradable or surface-functionalized nanoparticles should be prioritized. These "green" NPs should balance reactivity with environmental stability and safety. Second, field-scale monitoring systems must be established to track the fate, transformation, and bioavailability of NPs post-application. Lastly, the development of predictive risk assessment models that incorporate plant–soil–microbe–nano interactions is essential to guide policy and deployment. The future of NAPR lies in interdisciplinary integration—bridging nanoscience, soil microbiology, plant physiology, and environmental toxicology. With rigorous scientific validation and responsible innovation, NAPR has the potential to become a cornerstone technology in the restoration of metal-contaminated ecosystems.

Table: Enhancement Mechanisms in Nanoparticle-Assisted Phytoremediation

Enhancement Type	**Underlying Mechanism**	**Key Studies**
Metal mobilization	Nanoparticles lower pH or redox potential to release metals	Feizi et al., 2018
Root morphology	Induce lateral root growth, increasing uptake surface	Rajiv et al., 2018
Transporter activation	Upregulate ZIP, NRAMP, HMA genes via signaling cascades	Barabasz et al., 2019
Antioxidant defense	Boost SOD, CAT, APX activity to mitigate ROS	Saidi et al., 2014; Tripathi et al., 2017
Microbial synergy	Promote PGPR colonization and siderophore activity	Marques et al., 2013

Plant Growth Promoting Rhizobacteria (PGPR)

PGPR are beneficial microbes that colonize the rhizosphere and stimulate plant growth and stress resistance. Their functions relevant to phytoremediation include:

Function	**Mechanism**
Metal solubilization	Release of organic acids and siderophores
Growth hormone production	Synthesis of auxins (e.g., indole-3-acetic acid), gibberellins
Stress mitigation	ACC deaminase activity reduces ethylene levels under metal stress
Antioxidant regulation	Induce systemic resistance and antioxidative enzyme production

5. INTEGRATION STRATEGIES FOR ENHANCED PHYTOREMEDIATION

The synergistic integration of biological and nanotechnological tools presents a promising frontier in phytoremediation science. Recent advances suggest that combining plant growth-promoting rhizobacteria (PGPR), chelating agents, and engineered nanoparticles (NPs) can overcome the limitations of conventional approaches, leading to improved metal bioavailability, enhanced plant resilience, and minimized environmental risk. This section explores these synergies with mechanistic insights and case-based evidence.

5.1 Plant Growth-Promoting Rhizobacteria (PGPR)

PGPR are beneficial soil microbes that colonize the rhizosphere and contribute to plant growth and stress mitigation through multiple mechanisms. These include nitrogen fixation, phosphate solubilization, production of phytohormones such as indole-3-acetic acid (IAA), siderophore secretion, and modulation of ethylene levels via ACC deaminase activity. In phytoremediation contexts, PGPR enhance metal solubility and uptake, improve root development, and reduce oxidative stress.

5.2 Triadic Synergies: PGPR + Chelators + NPs

The strategic integration of PGPR, chelators, and nanoparticles offers a multifaceted approach to metal remediation. Each component contributes uniquely: chelators increase metal availability, PGPR mitigate toxicity and promote plant vigor, and nanoparticles enhance uptake efficiency while modifying the rhizospheric microenvironment.

He et al. (2017) provided compelling evidence of such synergy, demonstrating that Fe_3O_4–biochar nanocomposites loaded with photosynthetic bacteria improved Pb uptake in *H. annuus* by 60%. This treatment also increased chlorophyll content, reduced oxidative damage, and enhanced overall biomass, underscoring the potential of multifunctional remediation platforms. Similarly, Rajiv et al. (2018) reported increased antioxidant enzyme activity and shoot–root biomass ratio in sunflower following combined treatment with ZnO nanoparticles and foliar nutrient sprays.

5.3 Case Studies Demonstrating Integration Success

Study	Species	Combination Used	Key Outcomes
He et al. (2017)	*Helianthus annuus*	Fe_3O_4 + biochar + PGPR	↑ Pb uptake (60%), ↑ biomass (30%), ↓ oxidative stress
Lacalle et al. (2018)	*Zea mays*, *Sorghum*	Zero-valent Fe NPs + citric acid	↑ Zn/Cu uptake, ↑ microbial activity, improved antioxidant responses
Marques et al. (2013)	*Helianthus annuus*	PGPR + EDTA	↑ Cd/Zn uptake, ↑ stress tolerance, ↑ chlorophyll and shoot growth
Rajiv et al. (2018)	*Helianthus annuus*	ZnO NPs + foliar nutrient spray	↑ antioxidant enzymes, ↑ shoot-to-root ratio, improved physiological robustness

These studies illustrate how integrated systems can outperform standalone strategies, particularly under conditions of complex contamination or abiotic stress.

5.5 Soil and Environmental Considerations

The effectiveness of integrated remediation strategies is strongly modulated by soil type, pH, organic matter, and cation exchange capacity (CEC). Chelators tend to be more effective in sandy soils where metal mobility is higher, while clay-rich soils buffer NP movement and may reduce metal solubility (Feizi et al., 2018). Therefore, site-specific assessments of soil texture and composition are essential prior to deployment. Moreover, long-term environmental considerations must be factored into strategy design. For instance, while biochar-based nanomaterials improve soil carbon sequestration and microbial health, synthetic chelators like EDTA may persist in soil and mobilize metals beyond the target zone. The balance between remediation efficacy and environmental safety requires a careful selection of materials, application rates, and monitoring protocols.
pH: Chelator effectiveness and NP solubility are pH-dependent.
Organic matter: Binds chelates and NPs, reducing bioavai

6. RISKS AND ENVIRONMENTAL CONCERNS IN NANOPARTICLE-ASSISTED PHYTOREMEDIATION (NAPR)

While NAPR represents a technologically advanced solution to soil metal contamination, its implementation raises significant environmental and ecological concerns. Uncontrolled or poorly regulated application of nanoparticles may lead to unintended consequences, particularly in terms of soil microbial health, plant toxicity, food chain safety, and regulatory oversight. This section outlines key risks associated with NAPR and explores mitigation strategies based on current evidence and sustainable design principles.

6.1 Toxicity to Soil Microorganisms and Enzymes

Soil microbial communities are essential for maintaining nutrient cycling, organic matter decomposition, and heavy metal transformation. However, several studies have demonstrated that engineered nanoparticles, particularly at higher concentrations or prolonged exposure, can adversely affect microbial structure and function.

6.2 Plant-Level Toxicity

While low concentrations of nanoparticles can stimulate plant antioxidant defenses and improve stress tolerance, excessive exposure often results in phytotoxic effects that negate the benefits of NAPR.

Nanoparticle	Toxic Dose Range	Observed Effects
ZnO	>100 mg/kg soil	Chlorosis, membrane damage, reduced root elongation
Fe_3O_4	>150 mg/kg soil	Induced oxidative stress, lipid peroxidation
TiO_2	>200 mg/kg (foliar spray)	Disruption in photosynthesis, DNA damage

For example, Rajiv et al. (2018) demonstrated that ZnO NPs enhanced *Helianthus annuus* growth at 50 mg/kg, but application at 200 mg/kg led to reduced biomass and elevated oxidative stress biomarkers. These dose-dependent effects necessitate careful optimization of NP concentrations to avoid yield losses and environmental harm.

6.3 Bioaccumulation and Food Chain Transfer

One of the more contentious aspects of NAPR is the potential transfer of nanoparticles and mobilized metals into edible plant tissues, with implications for food safety and ecological bioaccumulation. Case studies in wheat and rice systems have shown that co-application of ZnO NPs and Cd not only improved Zn uptake but also increased Cd concentrations in harvested grains (Rizwan et al., 2019; Bashir et al., 2018). This raises serious concerns about metal–NP interactions enhancing the bioavailability of toxic elements in food crops. Moreover, NPs released into soil may leach into water systems or be translocated across trophic levels through herbivory and predation, further amplifying ecological risks.

6.4 Risks of Chelator–Nanoparticle Synergy

Chelating agents such as EDTA and citric acid are frequently co-applied with nanoparticles to enhance metal mobilization. However, their combined use can exacerbate environmental risks. Studies have shown that chelator–NP combinations increase the leaching potential of heavy metals, facilitate NP mobility across the soil–water interface, and destabilize colloidal suspensions, leading to unpredictable aggregation and transport behaviors (Lacalle et al., 2018). These effects can undermine the containment efficacy of phytoremediation and contribute to off-site pollution, especially in sandy or porous soils.

6.5 Regulatory and Monitoring Gaps

Despite the growing application of NPs in agriculture and remediation, their regulatory oversight remains fragmented and inconsistent across jurisdictions.

6.6 Strategies for Risk Reduction

A proactive approach to NAPR safety involves the deployment of specific mitigation strategies tailored to different risk categories.

Risk Type	Mitigation Strategy
Soil microbial toxicity	Use of biodegradable NPs; nanoencapsulated formulations
NP leaching and mobility	Application of slow-release carriers and surface-functionalized NPs
Food chain contamination	Restrict use to non-edible crops; adopt post-harvest bioenergy conversion
Bioaccumulation	Implement crop rotation to dilute residual NP presence
Regulatory uncertainty	Develop nanomaterial-specific EIAs and policy frameworks

6.7 Sustainable Design Principles: Toward Safe-by-Design Nanomaterials

To align with environmental safety and sustainability goals, recent research has emphasized the concept of "Safe-by-Design" nanomaterials—engineered to maximize remediation efficacy while minimizing unintended ecological consequences.

Innovative approaches include the use of surface coatings such as biopolymers or citric acid to reduce NP leaching and toxicity, and the incorporation of controlled-release systems like mesoporous silica or hydrogel matrices. Furthermore, green synthesis techniques that employ plant extracts or microbial templates offer an environmentally benign alternative to chemically synthesized NPs.

For example, Priyanka and Venkatachalam (2016) reported that biofabricated ZnO NPs derived from algae-based phycomolecules exhibited improved biocompatibility and significantly lower toxicity to beneficial microbes, supporting their use in soil systems with minimal disruption.

Table: Risk Pathways and Mitigation Framework

Risk Category	Primary Concern	Mitigation Recommendations
Soil microbial health	Enzyme inhibition, microbial diversity loss	Use eco-safe, biodegradable NPs; control application dosages
Food chain contamination	Uptake of metals and NPs in edible tissues	Limit NAPR to non-edible crops; monitor post-harvest residues
Groundwater leaching	Increased mobility due to chelator–NP synergy	Apply slow-release carriers and buffer zones
Regulatory gaps	Lack of harmonized global standards	Establish nanomaterial-specific EIA and legal definitions
Long-term ecosystem impact	Soil community shifts, trophic transfer	Conduct full life-cycle analyses and ecological impact assessments

7. CONCLUSION AND FUTURE PERSPECTIVES

The escalating crisis of heavy metal contamination in terrestrial ecosystems calls for innovative, ecologically sustainable, and scalable solutions. Nanoparticle-assisted phytoremediation (NAPR) has emerged as a next-generation strategy that integrates advances in plant science, microbiology, and nanotechnology to overcome critical barriers in conventional phytoremediation—namely, low metal bioavailability, plant toxicity, and inefficient translocation. This review demonstrates that *Helianthus annuus* remains a model phytoremediator, particularly when enhanced by synergistic interactions with engineered nanomaterials, plant growth-promoting rhizobacteria (PGPR), and chelators. While ZnO, Fe_3O_4, and TiO_2 nanoparticles show considerable promise in enhancing metal uptake and plant resilience, their dose-dependent phytotoxicity, interactions with rhizospheric microbiota, and long-term environmental fate necessitate careful calibration and risk assessment. Key knowledge gaps persist, including the scarcity of standardized comparative metrics, limited long-term and field-based studies, and inadequate understanding of nanoparticle behavior in complex, real-world soils. The lack of regulatory harmonization and insufficient monitoring frameworks further impede the safe and scalable deployment of NAPR technologies. To transition NAPR from experimental systems to field-scale solutions, future research must focus on: **Eco-design of biodegradable and safe-by-design nanomaterials, Multi-omics approaches** to understand species-specific responses, **Field trials across diverse agroecosystems, Life-cycle and risk assessments integrated into regulatory pipelines,** Ultimately, the successful adoption of NAPR depends not only on technological innovation but also on interdisciplinary collaboration, inclusive policy frameworks, and societal acceptance. When implemented responsibly, NAPR holds the potential to restore metal-contaminated lands, contribute to circular bioeconomies, and align remediation practices with the United Nations Sustainable Development Goals.

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