



REVIEW ARTICLE

Heavy metals in agroecosystems: Sources, soil contamination processes, plant uptake mechanisms and remediation approaches

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Abstract

The purpose behind critically analyzing the sources, pathways and ecological effects of heavy metal contamination in agroecosystems is to synthesize the available research in order to learn the important mechanisms of contamination and evaluate their effects on soil health, plant uptakes and food safety. Based on the latest scientific literature, the review discusses industrial processes as sources of cadmium, lead, arsenic, mercury, chromium, copper and nickel to the wastewater, including mining, metal and battery production and fertilizer production and also considers the contribution of municipal solid waste and sewage. With little over 30-40 % of the wastewater receiving proper treatment, there has been a massive release of untreated effluents to the natural water bodies and agricultural systems, posing persistent contamination threats. The review has placed importance on the fact that when polluted water is used in irrigation, it brings the heavy metals to soils and forms permanent complexes with the clay and organic matter, changing the soils structure, nutrient availability, microbial activity and general fertility. A thematic review of the available literature demonstrates that the bioavailability of heavy metals has been affected by the soil pH, redox potential and organic matter, which allows plants to uptake it via mass flow and diffusion and later translocation to edible tissues. This pollution of food is a great threat to human health, such as organ damage and neurological diseases. The review also assesses the existing mitigation strategies, including wastewater treatment, sustainable irrigation methods and soil remediation methods with special consideration to the potential and limitations of phytoremediation. It ends by providing research gaps and the necessity of long-term, ecosystem-level research studies to enhance plant-based remediation measures and agroecosystem resilience.

Keywords: crop uptake; heavy metals; human health; soil fertility; wastewater

Introduction

The problem of heavy metal pollution in agricultural soils has become a major environmental issue of concern in the world today due to the high rate of urbanization and increased agricultural activities. These components are chronic and not biodegradable and thus they end up building up in the soils and biota over time. Consequently, the heavy metals interfere with the ecosystems operation and become a tremendous threat to environmental sustainability and food security. The soils in agriculture are especially susceptible due to their long-term trapping of pollutants that are contributed by industrial emissions, mining, agrochemicals and wastewater irrigation and inappropriate disposal of waste. The existence of heavy metals in

agricultural land compromises the quality of the soil, disturbs microbial functions, diminishes food production and contributes to the process of transferring the toxic substances into the food chain. By biomagnification, the concentration of metals increases with an increase in trophic level, which eventually endangers human health.

The heavy metals are typically considered the screens, which have a density that is more than 5 g cm⁻³ or that have an atomic number that is more than 20 and are considered ubiquitous environmental pollutants (1). Cadmium (Cd), lead (Pb), chromium (Cr), arsenic (As), mercury (Hg), nickel (Ni), copper (Cu) and zinc (Zn) are the most common metals that have been reported to be present in contaminated soil. Of them, Cd, Pb, As,

Hg and Cr are especially dangerous, as they have phytotoxic as well as toxic effects even at comparably low levels (2-7). Certain metals like copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), Molybdenum (Mo), nickel (Ni), calcium (Ca), magnesium (Mg) and boron (B) (Fig. 1) are vital micronutrients needed in plant normal growth and development. They are involved in crucial physiological and biochemical processes in the right proportions, such as enzyme stimulation, photosynthesis, respiration, fixation of nitrogen, ion homogenization and expression of genes. Nevertheless, over-accumulation of all these otherwise vital components causes metabolic impairment, growth retardation and loss of yield and their deficiency causes typical nutrient stress responses.

The toxicity of the heavy metals and their persistence in soils is because they are not easily degraded by microbes or altered through chemical reactions and consequently, the heavy metals can persist in soils, just as they are found in the soil matrix, until they are taken up by plants, washed away during leaching or through remediation measures (2-4). Considering their long stability and the possibility of impact on ecological and human health, heavy metal pollution is one of the urgent concerns of agroecosystems in the world. Such knowledge gaps have been dealt with in this review by looking at the origin of heavy metals in agricultural soils, how they affect the health of soil and plant systems, how they are transferred to the food chain and their effects on human health and also the success of mitigation and remediation measures that are available. To create sustainable strategies to deal with the contaminated soils and to safeguard the environment and human health, it is necessary to improve the knowledge of these interconnected processes.

Origin of Heavy Metals in Soil

Heavy metal contamination in soils has emerged as a major environmental concern due to its impacts on soil quality, crop productivity and human and animal health. Elevated concentrations of toxic metals can reduce soil fertility, impair biological activity and enter the food chain, posing serious health risks. Globally, an estimated 5 million sites now exceed safe limits for heavy metal concentrations, highlighting the scale and urgency of the problem.

Key heavy metals of concern

Soil pollution will often include the presence of various heavy metals such as mercury (Hg), cadmium (Cd), copper (Cu), zinc (Zn), nickel (Ni), lead (Pb) and arsenic (As), to name a few. Of all these, the chief heavy metals that the United States Environmental Protection Agency (EPA) finds to cause a high risk to the human body include mercury, cadmium, lead and arsenic, which are all known for being highly toxic and having serious effects.

Natural background inputs

Natural processes deliver small but constant concentrations of heavy metals into soils and these include parent material weathering, volcanic activity and deposition of mineral dust. Natural background concentrations of metals such as nickel, chromium and zinc are introduced into soils through these processes. In nature, these concentrations are always relatively low and do not result in any ecological or health hazards.

Anthropogenic contributions

Current heavy metal contamination of soils is largely influenced by anthropogenic sources, with high deposition rates beyond natural background levels. These sources include agricultural inputs such as phosphate-based fertilizers and pesticides, animal manure and sewage slues; and industrial processes such as the production of heavy metals and their uses in electroplating and battery manufacturing and recycling; mining and smelting activities with high deposition rates of heavy metals into soil; as well as practices involved in waste disposal and irrigation of agricultural fields with sewage water. These practices significantly increase heavy metals in agricultural and peri-urban soils.

Mechanisms of soil entry and accumulation

Heavy metals can enter agricultural as well as urban soils in several different ways, such as irrigation of agricultural lands using contaminated or untreated wastewater, deposition from industrial emissions as well as from automobile exhausts in the atmosphere, runoff from industrial and mining areas through leaching or runoff into streams, as well as the use of fertilizers and pesticides that have impurities of trace heavy metal compounds in them. Once introduced, heavy metals persist in soils because they are non-biodegradable and readily adsorb onto soil minerals and organic matter, leading to long-term accumulation and limited natural removal.

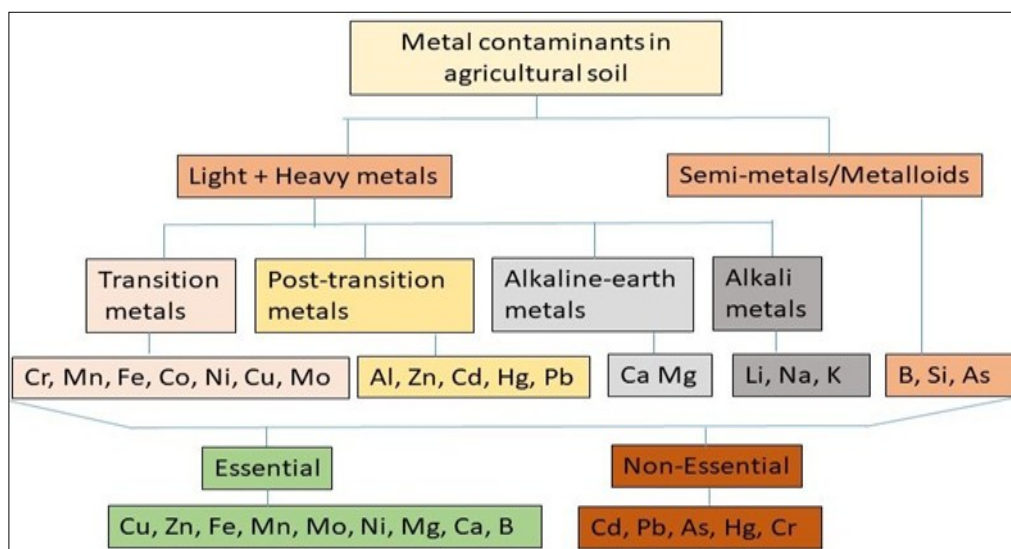


Fig. 1. Metal and non-metal elements that are commonly found in agricultural soils are categorised (19).

Natural sources

Natural sources of heavy metals in soils arise mainly from the weathering of igneous and sedimentary parent rocks, which gradually release trace metals into the soil through physical, chemical and biological processes. Volcanic activity further contributes metal-rich ash and aerosols containing elements such as Ni, Cr, Cu, Zn and Fe, while atmospheric dust deposition transports mineral particles that add baseline levels of metals like Ni, Cr, Zn and Mn. Collectively, these natural processes establish background heavy metal concentrations in soils, whereas elevated and widespread contamination is largely linked to anthropogenic activities.

Anthropogenic sources

Heavy metal concentrations in agricultural soils are significantly raised by anthropogenic sources, or those produced by human activity. Smelting, mining, burning fossil fuels for energy, disposing of municipal waste, application of fertilisers, pesticides and irrigating with sewage water are some of the anthropogenic activities leading to the accumulation of heavy metals (Fig. 2).

Industrial emissions and effluents

Industrial operations- mining, smelting, metal processing, manufacturing, coal and oil combustion and waste incineration by the release of heavy metals to the environment primarily through airborne emissions, industrial effluents, particulate deposition and contaminated waste disposal (8, 9). Common metals introduced include Pb, Ni, Cr, Hg, Cd, Cu, Zn and As.

Lead (Pb)- Mechanisms of soil entry: Lead enters soils mainly through atmospheric deposition from fossil fuel combustion, industrial emissions and waste incineration, as well as through runoff and leaching from lead-containing products such as paints, batteries, pigments, ceramics, explosives and PVC materials. Additional contamination occurs in areas affected by mining and metallurgical activities (10).

Nickel (Ni)- Mechanisms of soil entry: Nickel enters soils primarily via airborne particulates from coal combustion, mining and metallurgical industries, along with deposition from waste incineration, electroplating effluents and emissions associated with steel production and industrial aerosols (11).

Chromium (Cr)- Mechanisms of soil entry: Chromium enters soils mainly through industrial discharges from textile dyeing, electroplating, rubber and pigment industries, along with deposition

of dust and fumes from tanning, chemical manufacturing and residues from mining and metallurgical activities.

Mercury (Hg)- Mechanisms of soil entry: Mercury enters soils through industrial wastewater discharges and atmospheric emissions from fossil fuel combustion, as well as from fluorescent lamp waste, chemical manufacturing, industrial dust, agrochemicals and by-products of waste incineration.

Copper (Cu)- Mechanisms of soil entry: Copper enters soils via industrial effluents from textile processing, electroplating and pigment/paint production, as well as through runoff from mining and metallurgical activities, improper e-waste disposal and copper-based pesticide applications.

Arsenic (As)- Mechanisms of soil entry: Arsenic enters soils through emissions from mining, smelting and pharmaceutical/textile industries, discharge of industrial wastewater and fossil fuel combustion residues, use of arsenic-containing paints and pesticides and long-term application of phosphate fertilizers.

Cadmium (Cd)- Mechanisms of soil entry: Cadmium enters soils through mining and smelting activities, use of pigments, PVC products, pesticides and batteries, as well as deposition from industrial dust, waste incineration emissions and contaminated wastewater (12).

Zinc (Zn)-Mechanisms of soil entry: Zinc enters soils via galvanization, mining and metallurgical activities, electroplating, metal recycling, zinc-containing fertilizers and industrial particulate deposition.

Agricultural inputs

Agricultural practices introduce heavy metals into soil mainly through fertilizers, pesticides, livestock manures and composts, which deliver metals directly to the soil surface or root zone (13-16).

Fertilizers- Mechanisms of soil entry: Heavy metals enter soils through direct application of macro- and micronutrient fertilizers (Cu, Mn, Zn, Ni), contamination in phosphate fertilizers (Cd, Pb, Hg, F) and long-term overuse, causing accumulation in topsoil (17- 21).

Pesticides- Mechanisms of soil entry: Heavy metals enter soils via metal-based pesticide formulations (Cu, Pb, Hg, As, Mn, Zn), persistent residues from fungicides like Bordeaux mixture and copper oxychloride and localised contamination from arsenic-based pesticides and CCA-treated timber sites (22, 23).

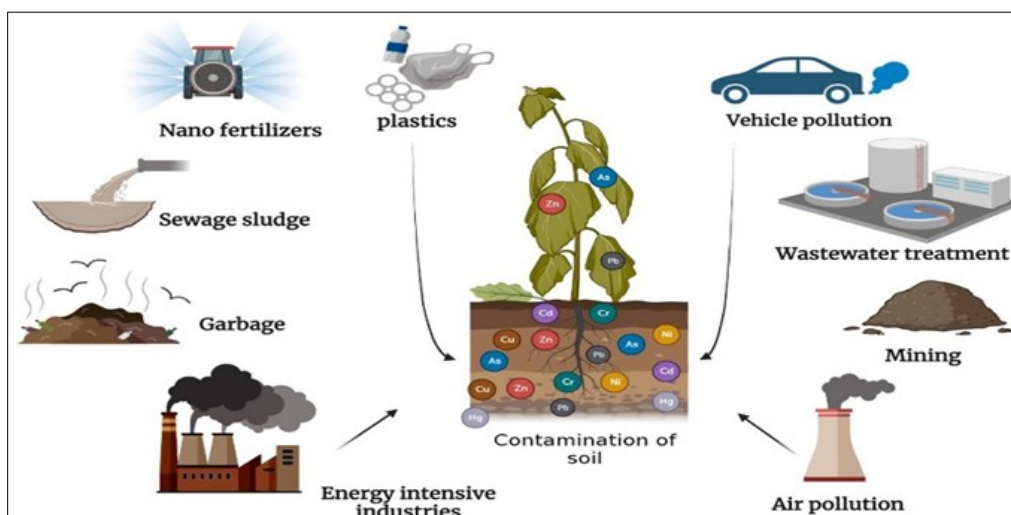


Fig. 2. HMs sources including plastics, mining, sewage, garbage, vehicles and nanofertilizer .

Livestock manure and compost: Mechanisms of soil entry: Heavy metals enter soils through direct application of manures enriched with minerals in animal feeds (Zn, Cu, As, Cd, Ni, Cr, Pb, Hg). These metals persist during composting and accumulate over repeated applications, potentially causing phytotoxicity and transfer through the food chain.

Wastewater and sewage sludge

Wastewater irrigation and sewage sludge application introduce metals to soil through direct spreading of treated/untreated sludge, infiltration and irrigation water.

Sewage Sludge / Biosolids: Mechanisms of soil entry: Heavy metals enter soils via direct application of sewage sludge containing As, Cd, Cr, Cu, Pb, Hg, Ni, Mo and Zn. Use of the untreated sludge has resulted in the accumulation of metals in the long run, especially in developing countries. Use of the treated biosolids has several benefits, including improvement in soil fertility. However, trace metals are present in biosolids. This is a widespread practice all over the world. In the U.S., 3 million dry tons are used. In Europe, over 30 % of processed sludge is applied.

Biochar and Heavy Metal Pollution

Biochar is increasingly used to mitigate metal contamination through adsorption, complexation and long-term stabilization. Biochar's durable structure makes it a sustainable strategy for lowering heavy metal bioavailability while enhancing agricultural productivity (24).

Mechanism of action: High surface area and functional groups immobilize metal ions. Stable carbon structure resists rapid decomposition compared to ordinary organic matter (25, 26). Reduces metal mobility and plant uptake, improving soil quality and crop safety.

Conditions for effective use: High sorption capacity across diverse environmental conditions. Long-term stability and functionality within soil ecosystems. (27, 28).

Impact of Heavy Metals on Soil

Heavy metals profoundly affect the biological, physical and chemical properties of soil as a complex phenomenon. Toxic heavy metals include Cd, Pb, Hg, Cu, Ni and Cr, which affect microbial processes, result in soil structure instability and affect major chemical reactions, hence leading to reduced soil fertility and soil biological functionality.

Impact of heavy metals on soil microbial communities

Agricultural, industrial and mining activities release heavy metals (e.g., Cd, Pb, Hg) that alter microbial communities that play an important role in nutrient cycling and in the turnover of organic matter. They cause cell membrane damage, enzyme inhibition and reduction in biomass, activity and diversity of microorganisms, damage decomposition, nitrification, denitrification and degradation of pollutants (Table 1). The microbial responses are inhibited metabolism, reduced nutrient mineralization and changed symbiosis between microbes and plants and mycorrhizal fungi (Fig.

Table 1. Effects of heavy metals (HMs) on soil properties

Metal	Primary soil effect	Mechanistic pathway	Key enzymes affected	References
Zinc (Zn)	Phytotoxicity; reduced soil fertility; decline in microbial biomass; reduced P availability	Excess Zn disrupts microbial cell metabolism and nutrient balance, inhibiting microbial growth and nutrient mineralization.	Dehydrogenase, phosphatase (general inhibition)	(29)
Lead (Pb)	Reduced soil productivity; nutrient imbalance (notably P); altered microbial metabolism	Pb binds to sulfhydryl (-SH) groups of enzymes, interferes with mineral nutrition, water balance and microbial metabolic pathways	Invertase, acid phosphatase, urease and catalase	(30, 31)
Copper (Cu)	Decline in N-cycling microorganisms; reduced soil N and S availability	Cu toxicity suppresses microbial biomass and enzyme synthesis, disrupting C, N and S cycling	β -glucosidase (strongly), cellulase (comparatively less)	(32)
Mercury (Hg)	Altered microbial metabolism and soil biological activity	Hg forms stable complexes with proteins, inhibiting enzymatic reactions and microbial respiration	Dehydrogenase, catalase (general inhibition)	(33, 34)
Cadmium (Cd)	Reduced soil fertility; impaired N and S availability; microbial stress	Cd induces oxidative stress and binds to enzyme active sites, inhibiting microbial metabolism	Urease, proteases, alkaline phosphatase	(29, 35)
Nickel (Ni)	Suppressed microbial growth; altered nutrient cycling	Excess Ni disrupts metalloenzyme function and microbial respiration	Dehydrogenase, urease	(33, 34)
Chromium (Cr)	Reduced microbial activity and soil biochemical functioning	Cr (especially Cr(VI)) induces oxidative stress and inhibits enzyme synthesis	Dehydrogenase, phosphatase	(32, 33)
Arsenic (As)	Impaired microbial metabolism; reduced nutrient transformations	As interferes with ATP production and phosphate metabolism in microbes	Phosphatase, dehydrogenase	(31, 32)

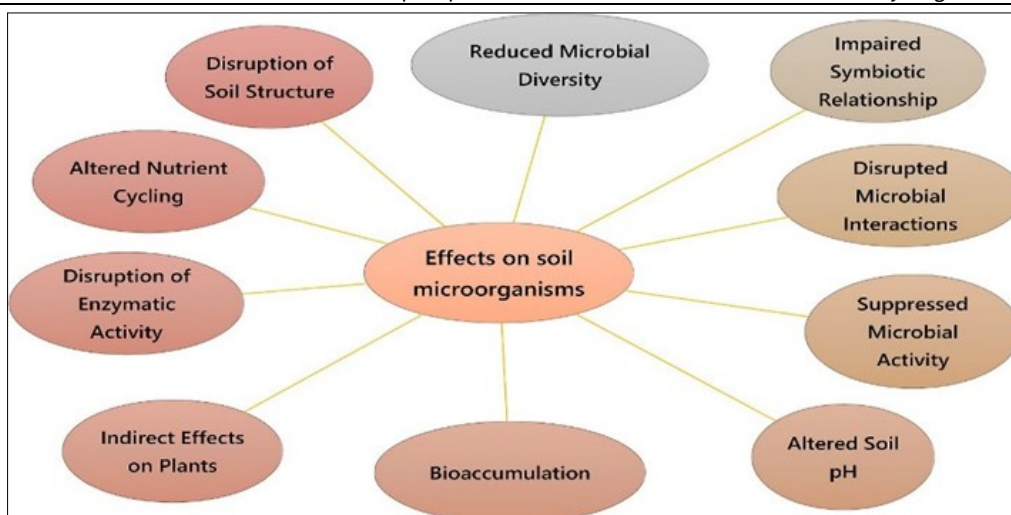


Fig. 3. Impact of heavy metals on soil microbes.

3). Others accumulate metal or become tolerant and the metals may be transferred down the food chain. These effects are controlled by the soil pH: Al and Pb decrease soil pH and Cu and Zn can slightly increase soil pH, changing the structure and activity of microbes. Cd, Cr and Zn have specific effects- they reduce the biomass and earthworm activity, bacteria metabolism and fungi arbuscular mycorrhizal, respectively. Microbial disruptions are therefore sensitive and early warning signs of heavy metal stress that initiate cascading impacts on the soil quality.

Impact on soil physical attributes

Metallic elements (Pb, Cd, Cu, Zn, Ni, Cr) affect the microbial activity by impairing it, reducing the aggregation of soil and weakening the physical structure. Key effects include:

Aggregate destabilization: Reduced microbial polysaccharides and fungal hyphae cause compaction.

Texture modification: Metal accumulation alters sand, silt and clay distribution.

Lower porosity and water-holding capacity: Clogged pores restrict air, water and nutrient movement.

Increased erosion risk: Weak aggregates heighten susceptibility to wind and water erosion.

Impact on soil chemical characteristics

Heavy metals drive chemical changes that interact with soil biology and physics:

pH modifications: Cd and Al acidify soils; Ni and Cr may increase alkalinity, affecting solubility and nutrient availability.

Nutrient imbalance: Pb, Zn and Ca compete with Mg, Fe, Mn and Ca, reducing plant and microbial efficiency.

Soil organic matter dynamics: Inhibited microbial decomposition (Zn, Cu, Cd) slows SOM breakdown, decreasing nutrient mineralization and carbon cycling.

Redox alterations: Metals affect Fe, Mn, N and S redox reactions, influencing nutrient mobility.

Adsorption/desorption: Metals strongly bind to clay and organic matter, limiting immediate bioavailability but allowing remobilization under pH or redox changes.

Revised Heavy Metals absorption mechanism in Plants

Numerous scientists have conducted research into the manner in which plants absorb contaminants. To improve the mechanism of plant uptake, it could be helpful to regulate the contributing factors. Plants typically serve as both accumulators and excluders (36). Even when contaminants are concentrated in their aerial parts, accumulators continue to exist. In their tissues, the plants biodegrade or biotransform the pollutants into inactive forms. In theory, the excluders restrict the amount of contaminants that can enter their biomass.

Key drivers of uptake mechanisms

The key drivers affecting the uptake mechanism of heavy metals are depicted in Fig. 4-5. Understanding these elements can significantly enhance the plant's uptake performance.

Plant species

Effective phytoremediation of heavy metal pollution in soils is based on the selection of the right plant species, which is an environmentally friendly approach to contamination mitigation. Phytoremediation can be carried out by using the following: phytofiltration, phytoextraction, phytostabilization, phytovolatilization, phytodegradation and rhizodegradation (37, 38). The effectiveness is determined by the biochemical and physiological characteristics of the plants that influence the metal uptake, accumulation, detoxification, or immobilisation (37).

One of them is the introduction of hyperaccumulator species that tolerate and accumulate high metal concentrations and maintain enough. The main functional characteristics are high biomass stress, overexpression of metal transporters, efficiency in chelation and antioxidant defense (39). Examples include *thlaspi caerulescens* (Zn and Cd) and *pteris vittata* (As). Plant reactions to metals are diverse, ranging from growth retardation and high tolerance; hence, successful phytoremediation needs species that will grow in polluted soils and effectively accumulate and sequester metals without being incompatible with agronomic activities.

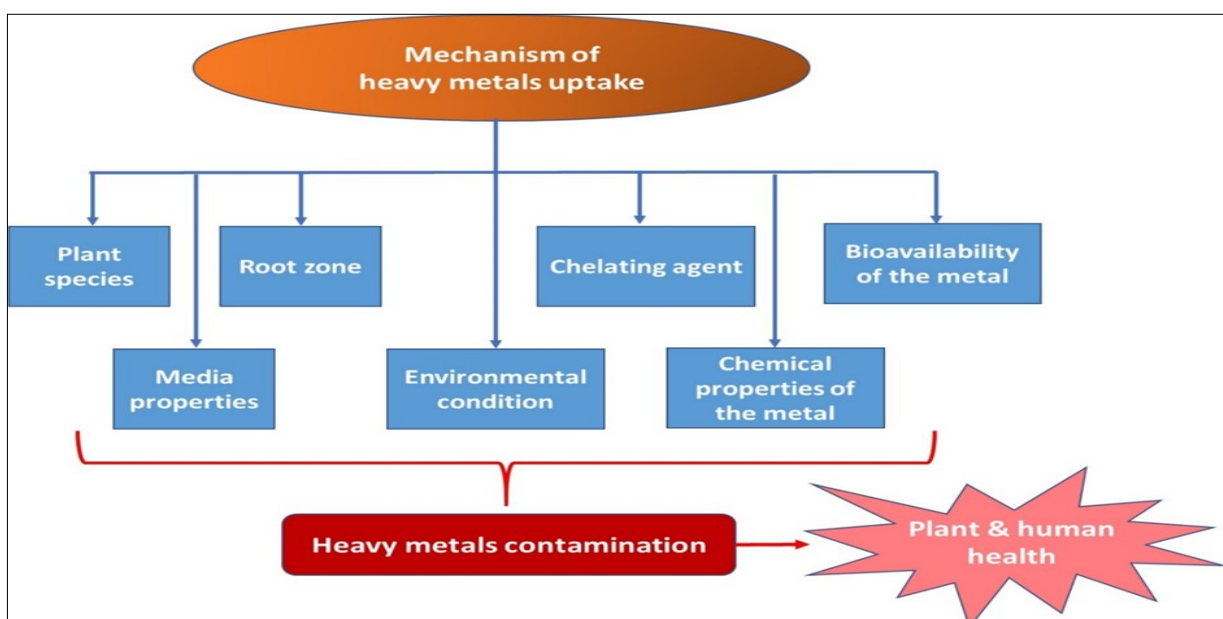


Fig. 4. Factors which are affecting the uptake mechanisms of heavy metals.

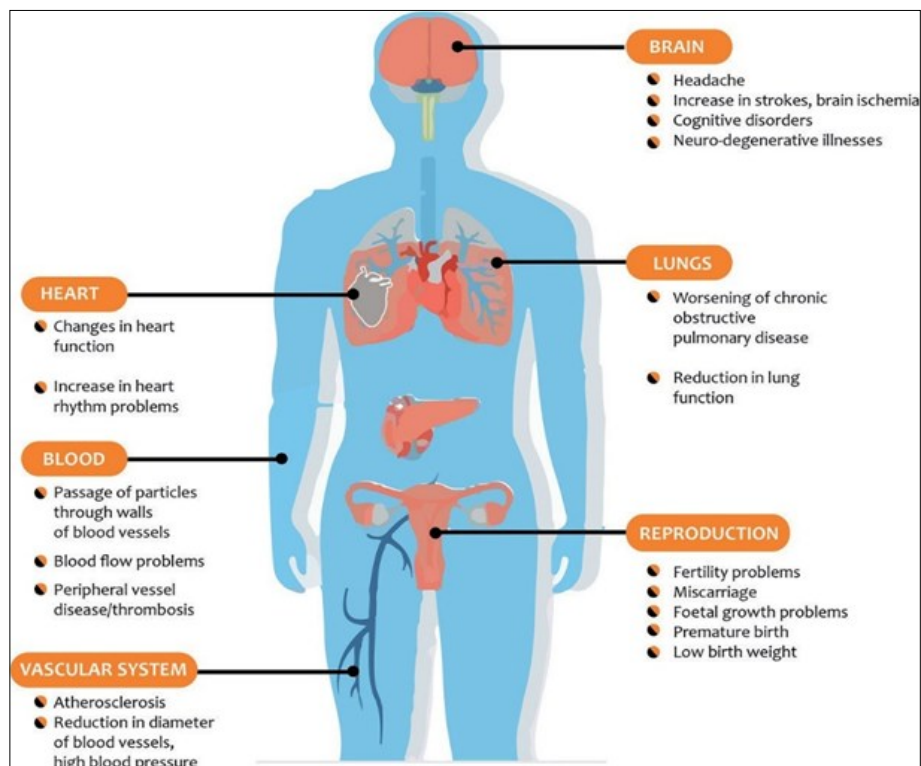


Fig. 5. Impact of heavy metals on various essential human organs.

The characteristics of the medium

Enhanced remediation through pH adjustment, the addition of chelators and the use of fertilisers under agronomic practices may influence metal uptake (40). The solubility of many heavy metals is strongly controlled by soil chemical conditions. When soil pH increases, metals tend to precipitate as hydroxides, carbonates, or phosphates, thereby reducing their mobility and availability to plants. Conversely, under acidic conditions, these metal compounds dissolve more readily, increasing the concentration of free metal ions in the soil solution.

As a result, soils are often adjusted to a pH of 6.5–7.0 to minimize lead uptake, as Pb becomes less soluble and more strongly bound to soil components within this range. Lead absorption is additionally affected by soil phosphorus content and organic matter, which can form stable Pb–phosphate and Pb–organic complexes that further reduce its bioavailability (41). Soil redox conditions also play a significant role: under reducing conditions, Fe and Mn oxides—key sorbents for heavy metals—may dissolve, releasing previously immobilized metals into the soil solution. Under oxidizing conditions, these oxides reform and can re-adsorb metals, influencing their mobility and uptake dynamics.

The root zone

The root zone forms the pivotal point of the phytoremediation process since it regulates the absorption, fixation and metabolism of pollutants in plant systems. Root tissues absorb, store or metabolise pollutants and the surrounding rhizosphere, which is full of microorganisms, further increases the rate of degradation. These microorganisms play an active role in the process of phytodegradation and rhizodegradation, which is promoted by carbon sources of plants and is overall involved in the degradation of contaminants in the soil (38).

Root exudates are important in the mechanistic processes of metal mobilization and uptake. Organic acids, amino acids, sugars and phenolic compounds are found that can chelate

metals, or may undergo a ligand-exchange reaction, substituting weaker ligands on soil colloids with stronger root-derived chelators. This increases the bioavailability of some of the metals to uptake or stabilization, as per the plant strategy. Exudates can also alter the local chemical environment of the rhizosphere in a very localized area, allowing target metals to be solubilized locally without extensive changes in soil chemistry. Morphological response among plants in the root zone also occurs under stressful conditions. Repeated drought causes plants to adapt, which causes the root diameter to increase and the elongation to reduce to ensure the plant continues to acquire water and minerals (42).

Vegetative uptake

The uptake of heavy metals by plants, which is fundamental to phytoremediation, is regulated by the environment as well as the structure and physiology of the plants. Temperature regulates the growth substances and controls root elongation, whereas root structure may differ significantly in the field and in controlled greenhouse settings, in contact with polluted areas of the soil (43, 44). Effective phytoextraction thus requires the use of hyperaccumulator species, which are specific to contaminants and knowledge of the mass balance and intracellular metabolic changes of pollutants (45, 46). After the metals get into the root system, they move to shoots through the presence of membrane transporters, chelation in the root cells, loading into the xylem and the effectiveness of long-distance translocation routes. Uptake efficiency is ultimately determined by metal bioavailability in the soil solution, which is determined by the retention processes, soil interactions and parameters like pH, redox potential, the levels of organic matter and the strength of binding the metals to the soil. Plants may also alter the immediate rhizosphere chemistry by changing the pH or by oxygenating the surrounding sediment, which affects the solubility and mobility of metals. Biodegradable chelating agents and micronutrients can further be used under controlled conditions to improve bioavailability and consequent translocation (47, 48).

Revised the chelating agent

Chelating agents promote the phytoremediation process mainly by making the heavy metals more biologically available and enabling their passage through the soil and into the plant tissues, thereby enhancing the movement of root to the shoot (49). Metal uptake efficiency can also be enhanced by biodegradable chelators and root-associated microbial activity, which can cut back the remediation time and costs. Chelators are especially needed in alkaline soils (pH > 5.560) and the solubility of the metals and their availability to plants is naturally low. The chelating agents enhance the movement of metals in the rhizosphere by creating complexes with the metals and assist in loading and transporting them upwards. Long-term use of synthetic chelators like EDTA has been found to stimulate internal metal translocation and the overall phytoextraction efficiency (50).

Nevertheless, synthetic chelators also have a possibility of augmenting the danger of leaching metals out of the root zone and controlled application tactics are required. By comparison, naturally occurring chelators, such as root-exuded organic acids, such as citrate and oxalate, regulate metal availability on a smaller scale and promote controlled uptake and translocation. Phytoextraction efficacy is thereby enhanced through the use of Chelate-assisted phytoremediation agents like NTA and EDTA which adjust the solubility and transport interactions of the metals and which also affect the relationship between plant uptake and possible off-site metal transfer (51).

Quantitative Assessment Metrics

Some of the quantitative parameters that are commonly used to assess the movement, uptake and internal distribution of heavy metals in plants include Bioaccumulation Factor (BAF) and Translocation Factor (TF). These markers can be used to estimate the bioavailability of metals in soils, risk factors related to the intake of crops and the appropriateness of plant species that can be used in phytoremediation. Although both indices are very useful tools, they possess limitations that one must interpret carefully.

Bioaccumulation Factor (BAF)

The Bioaccumulation Factor (BAF) is used to express the potential of soil to transfer metals to plants, usually in rice (52). It measures the concentration of heavy metals that are in soil in edible tissues in plants.

Bioaccumulation factor (BAF) = Concentration of metal in rice grain (mg/kg) / Concentration of metal in soil (mg/kg) (Eqn.1)

$$\text{BAF} = Cr / Cs \quad (\text{Eqn. 2})$$

where Cr and Cs represent metal concentrations (mg/kg, dry weight) in rice grains and soil, respectively.

A BAF less than 1 shows uptake, but no major accumulation, whereas a BAF greater than 1 shows a high potential of accumulation (53, 54). Hyperaccumulators (retaining metal at levels exceeding 1 mg/kg in aerial tissues without being phytotoxic) and excluders (localizing most metals to root tissues, with limited translocation to shoots) have been proposed based on the classification (55, 56).

Limitations

The values of the BAF are susceptible to changes in the soil heterogeneity, the specificity of plant organs, the stage of development and low levels of the soil metal that can artificially

deflate ratios (57-58). Therefore, BAF is the most dependable when used together with physiological and environmental tests.

Translocation factor (TF)

Translocation Factor (TF) is a factor that measures the mobility of heavy metals within the plants, which denotes how effectively the plants move the metals between the roots and shoots or other above-ground organs (59). It is calculated as:

$$\text{TF} = Cs / Cr \quad (\text{Eqn. 3})$$

with Cs representing the concentration of metal in shoots and Cr representing the concentration of metal in roots or soil (60-62). $\text{TF} > 1$ is an indicator of efficient root to shoot transfer and is typical of hyperaccumulating species (63). An increase in TF values is associated with an increase in the metal mobility and bioavailability within the plant-soil system (64-66).

Limitations

TF is sensitive to plant physiology traits, environmental factors as well as spatial heterogeneity of the soil as well as variations relative to growth stage. At low levels of soil metals, TF values can be exaggerated in reflecting the actual translocation capacity.

Rhizosphere Chemistry and Heavy Metal Chelation

Rhizosphere - the thin soil layer that is affected by the root of the plant is central in controlling the movement of heavy metals (HM), bioavailability and their later uptake by the plant. The uptake of roots is also interwoven with the chemical interactions that take place in this zone, in which plants and microbes interactively alter the speciation of HM by means of chelation, ligand exchange and pH changes. In normal growth conditions, roots exude low-molecular-weight organic compounds (e.g., amino acids (e.g. methionine, lysine, histidine), organic acids (e.g., oxalic, citric, malic, tartaric, succinic acids)). These exudates create insoluble complexes with metal ions, which decreases their free ionic activity and, in turn, regulates their entry into root tissues. The role of chelation in the rhizosphere serves as an initial detoxification mechanism, which has an effect on the sorption of roots and subsequent translocation of the root to the downstream.

This response is improved by metal-induced stress. Indicatively, the tolerant rice varieties of cadmium (Cd), release organic acids that are at least two times those of the cadmium-insensitive varieties, enhancing external chelation and limiting the bioavailability of Cd (67). Similarly, non-crop species that come in contact with Pb, Zn, Cu and Cd release high amounts of oxalic and malic acids that reduce toxicity by forming ligands (68). Such chelating interactions have a direct effect on the root uptake processes by reducing the percentage of metals that are in readily accessible ionic forms.

There is yet another step of chemical transformation, which is presented by the rhizosphere microorganisms. The growth of various groups of bacteria and fungi through the carbon of roots also provides not only HMs but also metabolites, such as gluconic, oxalic, acetic and malic acid, which then combine with HMs, changing solubility (69, 70). This type of chelation is mediated by microbes, which supplement plant exudation, decreasing the amount of bioavailable metals to which the root moves. This plant-microbe complex regulates the HM partitioning of the soil, root apoplast and internal paths of transport.

Organ-Specific Toxicity of Heavy Metals in Humans

The main human exposures to heavy metals are food and drinking water. The air, water and soil have been highly contaminated with heavy metals due to the industrial and agricultural activities that have been ignited by globalisation, urbanisation and economic growth (71). This pollution causes bioaccumulation in the food chain, which ends up exposing human beings. Exposure to heavy metals has health effects depending on the concentration and duration of exposure (Fig. 6). The seventh most toxic metal is Cadmium (Cd), which causes oxidative stress and has carcinogenic and mutagenic effects. The long-term exposure may cause gross health problems, such as kidney damage, prostate dysfunction, bone diseases and cancer (72, 73).

Cadmium

Cd attacks the proximal tubular cells of the kidneys mainly and their functioning is hampered. This interference leads to a decrease in reabsorption of low-molecular mass proteins and vital nutrients that cause proteinuria, which is a sign of tubular malfunction. This is worsened by Cd-induced oxidative stress, which produces reactive oxygen species (ROS), which destroy cell membranes, proteins and DNA in renal cells. Furthermore, Cd disrupts the calcium metabolism of the body, disrupting the bone homeostasis and leading to osteomalacia and other skeletal diseases. The health effects of arsenic (As) exposure are linked to a broad range impact that depend on the type of chemical, dose and exposure duration. The toxicity of inorganic arsenic (especially arsenite [As(III)]) compared to arsenate [As(V)] is associated with its greater reactivity and uptake by the cells.

Skin and integumentary system: Repeated exposure to As may result in skin lesions, hyperpigmentation, keratosis and risk of skin cancers (74).

Heart: Prolonged exposure is associated with high blood pressure, narrowing of the blood vessels and other circulatory disorders (75).

Neurological system: Arsenic may cause developmental abnormalities, neurobehavioral deficits, such as cognitive impairment and peripheral neuropathy.

Endocrine and hematologic effects: Exposure can cause diabetes-like metabolic imbalances, anaemia, leukopenia, eosinophilia and interference with normal hematopoietic activity (75, 76).

Carcinogenicity: Inorganic arsenic, particularly As(III), is suggested to cause skin, bladder, lung and liver cancers. The excessive level of As in the drinking water is one of the primary causes of chronic exposure, with the ultimate result of cumulative toxicity in the system of all organs.

Chromium (Cr)

Chromium (Cr) is a metal that exists in various oxidation states, where trivalent chromium [Cr(III)] is an essential micronutrient that plays a role in glucose and lipid metabolism and hexavalent chromium [Cr(VI)] is very toxic. The Cr(VI) has great potency to permeate cell membranes through the sulfate transport system, unlike Cr(III), which has a slow uptake in cells. After entering the cell, Cr(VI) is reduced intracellularly to Cr(III) to produce reactive oxygen species (ROS) and cause oxidative stress. This redox cycling contributes to DNA strand breaks, nucleic acid and protein denaturation, lipid peroxidation and breaking cellular signalling pathways. Repeated exposure to Cr(VI) may cause organ-specific toxicity (e.g., skin irritation and skin ulcers), respiratory (e.g., nasal irritation, lung inflammation, lung carcinoma) and neurological (e.g., hearing loss) impairments (73, 77, 78).

Lead (Pb)

Lead (Pb) exposure can induce a wide range of adverse health effects, affecting multiple organ systems.

Neurotoxicity: Pb interferes with neurotransmission and neuronal development, leading to decreased intelligence quotient (IQ), memory deficits, attention disorders, mood disturbances and behavioural changes. Pediatric populations are especially vulnerable due to an immature blood-brain barrier, which facilitates higher Pb accumulation in the central nervous system.

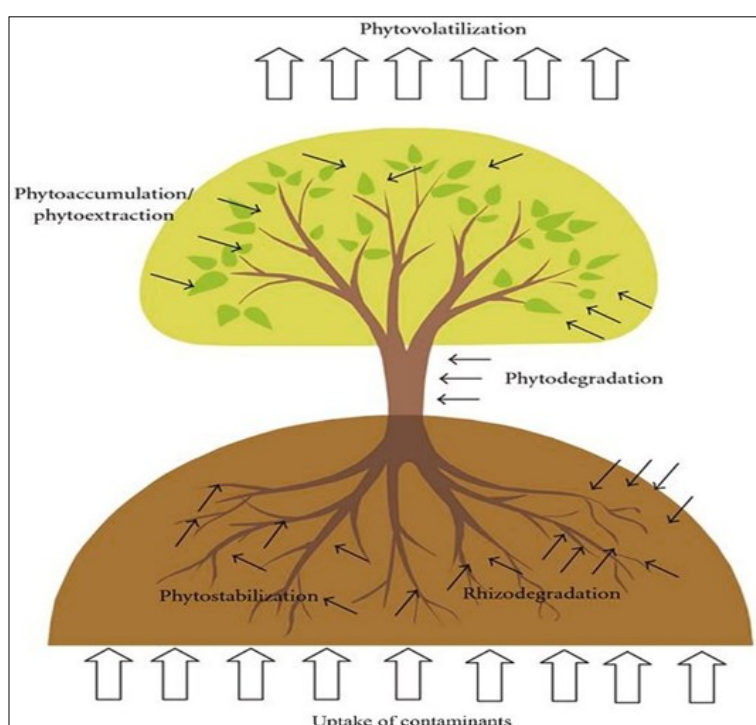


Fig. 6. Heavy metal uptake mechanisms of phytoremediation technology.

Renal toxicity: Chronic Pb exposure can impair kidney function, causing proximal tubular dysfunction and decreased renal clearance.

Hematological interference: Pb inhibits enzymes such as delta-aminolevulinic acid dehydratase (ALA-D), disrupting heme synthesis and resulting in anemia.

Reproductive effects: Pb exposure is linked to infertility, miscarriage and developmental abnormalities in offspring.

Mitigation Strategies

Phytoremediation of heavy metals in soil and water

Phytoremediation exploits the natural ability of metal-accumulating plants to remove, stabilize, or detoxify heavy metals in soil and water (79). This approach includes several processes, such as phytostabilization, rhizodegradation, phytoextraction, phytodegradation, phytoaccumulation and phytovolatilization (80) (Fig. 6 & Table 2).

The selection of phytoremediation for a contaminated site depends on several criteria: low-to-moderate levels of contamination, shallow soil depth and the suitability of non-food or marginal lands to prevent food chain contamination. While phytoremediation is environmentally friendly and cost-effective, it is a time-consuming process and generally less effective for metals that are strongly bound to soil particles or immobilized within soil matrices.

Phytoremediation techniques

Phytoextraction: Phytoextraction, also referred to as phytoaccumulation, phytoabsorption, or phytosequestration, is the process by which plant roots uptake heavy metals from soil and translocate them to above-ground shoots, enabling the removal of contaminants through harvesting of both roots and shoots (81-84). This approach has been successfully demonstrated across a variety of plant species. For example, twelve native plants grown on sludge were evaluated for iron (Fe) accumulation, with *Amaranthus spinosus* L. showing notable Zn and Mn accumulation in shoots. Except for *A. spinosus* L. and *Ricinus communis*, all tested plants displayed leaf accumulation of Fe, Mn and Zn (85). It has also been pointed out that ornamental plants can be used as a potential HM phytoextractant in contaminated sites and provide ecological advantages in comparison with the traditional remediation techniques (86). The research conducted on the growth of

vegetables in agricultural soils under refinery wastewater irrigation showed that Cd and Hg accumulated to a large extent in the edible tissues and this highlights the health risks (87).

The modern developments are directed at improving the phytoextraction efficiency. Such strategies as biodegradable chelator (e.g. EDDS ethylenediamine-N, N+disuccinic acid), agronomic amendment (ex, potassium salts, plant growth regulators, iron chelates) are used to increase bioavailability and uptake of Cd, Ni and Cu in such species as *Trifolium repens* (88). Moreover, breeding and selection programs in hyperaccumulator plants include the production of improved varieties of plants with the increase of metal transporter expression, biomass and resistance to high metal levels, which makes the phytoextraction potential more effective.

Phytostabilization: The concept of phytostabilization will be used to fix the heavy metals (HMs) in the contaminated soils with metal-tolerant plants to decrease their bioavailability and avoid leaching into the groundwater or entering the food chain (84, 89). Various factors affect the efficacy of phytostabilization such as root depth, soil amendments (e.g. organic matter, lime or biochar) and chemical speciation of the metals that determine their mobility and availability. An example is a study that evaluated four woody plant species in combination with organic amendments to stabilize the phytotransformation of zinc smelting slag and the authors found that the direct vegetation establishment enhanced the nutrient accumulation in the soils and also decreased the bioavailability of Cu, Zn and Cd (90). Equally, the aromatic plant, *Helianthus petiolaris*, indicated tolerance to Cd²⁺ at 500 mg/kg and Pb²⁺ at 500 mg/kg. The plant not only concentrated Cd in its aerial tissues three times above those of the soil but also translocated high amounts of Pb, which points to its ability to stabilize Cd (91).

Studies on the new macrophyte *Vossia cuspidata* in aquatic environments showed a considerable variation in levels of heavy metal (HM) accumulation in plant matter, with underground plant parts functioning as a principal retention component (92). These results underscore that successful phytostabilization must be carried out in collaboration with plant species selection and optimal rooting systems. The different metals' speciation conditions introduced in this paper were found to be important in relation to improved HM immobilization.

Table 2. Different phytoremediation processes for HM uptake

Technique	Mechanism	Suitable metals	Representative plant species	Advantages	Limitations
Phytoextraction	Uptake of metals via root transporters followed by translocation and accumulation in above-ground tissues (hyperaccumulation)	Cd, Zn, Ni, Cu and As	<i>Brassica juncea</i> , <i>Thlaspi caerulescens</i> , <i>Pteris vittata</i>	Cost-effective; permanent removal of metals from soil	Slow process; requires repeated harvesting and safe biomass disposal
Phytostabilization	Immobilization of metals in the rhizosphere through complexation, adsorption and root-induced precipitation	Pb, Cr, As, Cu and Zn	<i>Vetiveria zizanioides</i> , <i>Agrostis capillaris</i>	Reduces metal mobility and erosion risk; suitable for mine tailings	Does not remove metals; long-term monitoring required
Phytovolatilization	Uptake and transformation of contaminants into volatile forms released through leaves	Hg, Se and As	<i>Brassica juncea</i> , <i>Arabidopsis thaliana</i>	Reduces soil contaminant load without biomass disposal	Possible atmospheric redistribution; limited to specific elements
Rhizofiltration	Adsorption or precipitation of metals onto roots and rhizosphere surfaces	Pb, Cd, Cu, Zn and Ni	<i>Helianthus annuus</i> , <i>Eichhornia crassipes</i>	Effective for wastewater and aqueous systems; rapid uptake	Limited field application; requires root harvesting and disposal

Rhizofiltration: Rhizofiltration is a method of phytoremediation that uses plant roots to absorb and accumulate heavy metals in wastewater and industrial effluent (89). The effectiveness of this method is increased by root exudates that can act as chelators and adjust the pH of the rhizosphere and this increases solubilization and uptake of heavy metals. Rhizofiltration systems also have the possibility of being constructed using either hydroponic techniques or soil techniques. In hydroponic techniques, the plants are grown in nutrient solutions that enable direct contact between the roots of the plants and the contaminated water and hence are often associated with faster and larger removal of heavy metals. In soil rhizofiltration techniques, the plants are grown in soil that affects the uptake of the heavy metals, depending on the characteristics of the soil, like pH, organic matter content and cation exchange capacity, among others.

Research indicates that *Zea mays* effectively absorbs and accumulates mercury (Hg) from contaminated water (93). In a field study, *Phragmites australis* and *Kyllinga nemoralis* were evaluated at a municipal wastewater treatment facility in KwaZulu-Natal, South Africa, demonstrating significant differences in heavy metal concentrations between treated and untreated zones. Cd levels in the roots of *K. nemoralis* increased by 33% and 21%, respectively, highlighting its potential for effective phytoremediation (93-94). In general, the effectiveness of rhizofiltration is influenced by the species of plants, the root surface area, the characteristics of the water and the nature of the system (hydroponic compared to soil systems) and hydroponic systems are more effective compared to soil systems in the removal of heavy metals.

Phytovolatilization: Phytovolatilization is a kind of phytoremediation that involves a plant taking up a pollutant and converting it into a less toxic, volatile compound that is released into the atmosphere (89). This biotic technique has been implemented for organic

pollutants and a few heavy metals, such as selenium (Se), mercury (Hg) and arsenic (As). For instance, *Astragalus racemosus* can volatilize selenium by transforming it into dimethyl diselenide, *Arabidopsis thaliana* can volatilize ionic mercury (Hg^{2+}) by reducing it into its elemental form (Hg^0) and *Pteris vittata* can volatilize arsenic by transforming it into a vapor form (gaseous) (95, 96). Through this technique, a decrease in toxic elemental levels in soil and water can be achieved due to their conversion into volatile compounds. Despite this, this method has also generated debate, particularly since it can transfer pollutants from soil or water into the air, thus posing possible threats to ecological environments as well as humans. Risk assessment has, thus, become an essential step in understanding possible exposure of adjacent ecosystems or communities to particular species that can be volatilized. These include notions such as volatility, persistence and air dispersion, among others (97-107).

Even though the conventional physico-chemical techniques used for the removal of heavy metals from water and wastewater, such as ion exchange, coagulation, chemical precipitation, adsorption, membrane filtration and reverse osmosis, are effective and efficient, especially if the metal is above 2 mM, the techniques are limited by high costs and the generation of secondary waste. A combination of physical, chemical and biological techniques could provide better efficiency and effectiveness and could overcome the limitations of individual techniques. Even though a combination of techniques would provide better efficiency and effectiveness, better control and management are also required to counter or overcome the limitations associated with the techniques (Table 3).

Table 3. The benefits and challenges of heavy metal removal methods

Method	Effective for	Efficiency range	Key benefits	Key limitations	References
Oxidation	Heavy metals in contaminated soils and water	Moderate-high (process-dependent)	Accelerates the transformation and removal of heavy metals	High operational cost; formation of secondary by-products	(97)
Ion exchange	Wastewater and contaminated water containing multiple metals	High (up to 90-99%)	Efficient removal of a wide range of heavy metals	Resins require regeneration or safe disposal after saturation	(97, 98)
Ion-exchange resins	Industrial effluents, drinking water treatment	High ($\geq 95\%$)	High selectivity and reusability	High material cost; fouling reduces efficiency	(97, 98)
Chemical precipitation	Industrial effluents and wastewater	Moderate-high (80-95%)	Simple and effective for bulk metal removal	Generates large volumes of sludge requiring management	(99)
Adsorption	Water and wastewater containing trace metals	High (70-98%)	Simple, flexible design; resistant to metal toxicity	Adsorbent regeneration is needed to maintain performance	(100, 97)
Membrane filtration	Contaminated water and waste streams	Very high ($>95\%$)	High separation efficiency; compact systems	High operational cost; concentrated sludge/brine disposal	(101, 97)
Coagulation / Flocculation	Wastewater and industrial effluents	Moderate-high (70-90%)	Cost-effective and easy to operate	Produces bulky sludge requiring disposal	(97)
Electrocoagulation	Industrial wastewater with mixed metals	High (80-98%)	Reduced chemical use; effective for complex effluents	High energy demand; electrode passivation	(97)
Biological treatment	Polluted water and wastewater	Variable (60-90%)	Eco-friendly, cost-effective, sustainable	Limited large-scale commercialization	(103, 104)
Biochar immobilization	Agricultural and contaminated soils	Moderate-high (metal immobilisation $>70\%$)	Reduces metal mobility and bioavailability; improves soil quality	Does not remove metals; effectiveness depends on biochar type	(100, 102)
Nanomaterials	Water and wastewater with trace metals	Very high ($>95\%$)	High surface area; rapid adsorption kinetics	High cost; potential environmental risks	(101, 103)

Policy and Regulation: Guidelines for Wastewater Reuse in Agriculture

The reclaimed water is widely utilized in agriculture, as well as the irrigation of golf courses, public parks, urban greenbelts and lawn areas. China, Syria, Colombia, South Africa, Italy, Israel, the USA, Mexico and Chile are among those countries that have effectively utilized the reuse of wastewater, with many other countries adopting the same. The method helps in conserving water as well as meeting the needed nutrition. (Fig. 7). However, the reuse of treated wastewater poses possible dangers of heavy metal (HM) accumulation within the soil. The following are guidelines by international organizations and national standards concerning the permissible concentrations of heavy metals within the irrigational water for reduced contamination and uptake of cadmium (Cd): ≤ 0.01 mg/L, lead (Pb): ≤ 5 mg/L, copper (Cu): ≤ 0.2 mg/L, zinc (Zn): ≤ 2 mg/L, nickel (Ni): ≤ 0.2 mg/L, chromium (Cr): ≤ 0.1 mg/L, arsenic (As): ≤ 0.1 mg/L and mercury (Hg): ≤ 0.001 mg/L by crops.

Irrigation

Irrigation using water exceeding these HM thresholds can lead to gradual soil accumulation, altering soil physicochemical properties and increasing the risk of plant uptake, ultimately affecting food safety and human health. Therefore, continuous monitoring of HM concentrations in reclaimed water and soil, along with adherence to regulatory limits, is essential to ensure sustainable and safe agricultural reuse.

Industrial reuse

After irrigation, industrial use is the second-largest consumer of reclaimed wastewater. A number of industrial applications, like cooling and boiler feedwater, can function effectively using reclaimed wastewater without requiring high-quality water. Yet certain restrictions are applicable for industries that can be affected by corrosion, fouling and scaling. For example, if an industry is affected by corrosion, fouling and scaling, additional treatment processes like softening, demineralization, or filtration could be necessary.

Direct potable reuse (DPR)

Direct potable reuse (DPR) is the treatment of wastewater to a purity level where it can be incorporated in municipal water supply systems and consumed. The earliest DPR system was formed in Windhoek, Namibia, which happened in 1968. The implementation of DPR systems is still low because of the health safety of people, since untreated water may have pathogens and chemical pollution that will harm human health. Counter measures, like To avert these risks, DPR should be subjected to a multi-barrier treatment procedure, including reverse osmosis (RO), ultraviolet (UV) disinfection and advanced oxidation procedures (AOP) and provide extensive monitoring of water quality and safety. In spite of these issues, DPR is a good solution to areas with extreme water shortages.

Indirect potable reuse (IPR)

Indirect potable reuse (IPR) is the type of wastewater release to the ground, which replaces groundwater resources. This method is typically more publicly acceptable in comparison with DPR because natural soil filtration assists in getting rid of pathogens, lowering the concentration of contaminants and enhancing the quality of water. Some of the notable IPR projects are groundwater restoration and direct injection projects in Orange County, California; Fairfax, Virginia; and Singapore. The natural processes of soil or groundwater attenuation do not usually result in heavy metal accumulation, but to be sure that the long-term use is not based on the ecological and health hazards, monitoring is suggested.

Non-potable household and other domestic uses.

The treated wastewater may be safely utilized in non-portable domestic processes that include toilet flushing, cleaning and car washing, as well as in aquaculture, construction and maintenance of recreational water bodies such as lakes, ponds, etc. The applications assist in the conservation of fresh water. Overall, these applications would be low-risk of heavy metals, but it is recommended that periodic monitoring be conducted to avoid the possible development of heavy metals in soils or aquatic life.

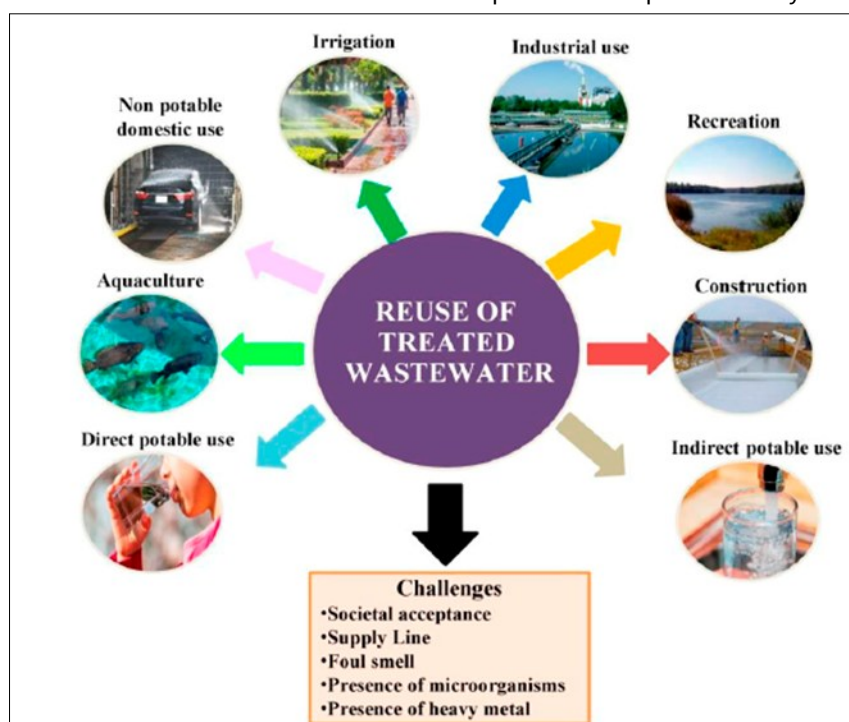


Fig. 7. Prospects and challenges in wastewater reuse.

Conclusion

The sources of heavy metals (HMs) are various, anthropogenic and industrial in nature, which cause the contamination of the soil and water with significant ecological implications. HMs in soils disrupt the microbial communities, change physical and chemical properties and reduce the nutrient availability. The ultimate clinical consequences include the growth and productivity of plants. HMs can be taken up and translocated by plants and consequently affect the food security and the health of humans by bioaccumulating. Long term HM exposure carries dangerous health risks such as neurotoxicity, renal dysfunction and organ-specific damage. Phytoremediation can be identified as one of the mitigation methods as it is a cost-effective and environmentally friendly technique and it uses metal-absorbing plants to stabilize, extract or volatilize contaminants. Though successful, phytoremediation needs to be selected with caution in terms of plant species, the issue of metal bioavailability and agronomic practices that support effective phytoremediation. In general, whole management, including the combination of source control, soil remediation, uptake of plants and mitigation of health risks, is a comprehensive approach to the contaminated environment with HM. To improve phytoremediation efficiency, innovative plant species must be used that are capable of removing heavy metals from polluted soils. In addition, techniques that make metals bioavailable—such as the use of bioaugmented, acidified manure, lower soil pH and hence increase the plants uptake of heavy metals." The development of genetic engineering and molecular techniques provides encouraging innovations for increasing the efficiency of phytoremediation, not only for restoring soil quality but also for recovering precious metal ions from heavily polluted areas. The combination of chelating agent and microbial applications has also improved the bioavailability of heavy metals to support their increased uptake by plants and speedy cleanup of soil contaminants. With the speed of urbanization and industrialization, the production of wastewater has increased. Hence, the treatment of wastewater has become essential before discharge. Recently, the focus has been on the treatment of wastewater, especially in reuse applications. Future studies should also focus on evaluating the effect of varying catalysts on phytoremediation and how this could improve its viability as a sustainable approach for restoration.

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Authors' contributions

KLP conceptualized the review topic, conducted an extensive and systematic literature survey, compiled and analyzed relevant information and prepared the initial draft of the manuscript. PVB and OVK contributed to literature screening, data organization and assisted in synthesizing information related to wastewater sources and heavy metal contamination. CR contributed to the collection, synthesis and interpretation of literature focusing on heavy metal

sources, soil contamination processes and crop uptake mechanisms. MC provided expert inputs on environmental pollution and soil contamination aspects and contributed to strengthening the discussion and interpretation of findings. BRI assisted in critically reviewing literature related to soil chemistry, nutrient-metal interactions and remediation strategies. TD contributed to evaluating the agronomic implications of heavy metal contamination and helped improve the clarity and flow of the manuscript. NR supported the interpretation of soil-plant interactions and enhanced methodological perspectives discussed in the review. SS contributed interdisciplinary insights and assisted with manuscript editing and formatting. AKP provided subject-specific inputs related to pest-soil-plant interactions under contaminated conditions and reviewed the manuscript for broader agricultural relevance. KPP contributed to improving conceptual clarity, logical organization and final proofreading of the manuscript. PVB provided overall supervision, refined the conceptual framework, guided the organization and structure of the manuscript and critically reviewed the content for scientific rigor, coherence and completeness. All authors read and approved the final manuscript.

Compliance with ethical standards

Conflict of interest: Authors do not have any conflict of interest to declare.

Ethical issues: None

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