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(Review Article)

Heavy metal contamination in agricultural soils: Sources, speciation and remediation strategies: A Review Journal Article

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Abstract

Heavy metal contamination of agricultural soils is a global environmental crisis threatening food security, ecological integrity, and human health. Source apportionment studies using receptor models reveal that anthropogenic activities including fertilizer and pesticide application, atmospheric deposition, industrial emissions, and sewage irrigation account for 65 to 86% of heavy metal accumulation in agricultural soils globally. Metal speciation, assessed through sequential extraction schemes and advanced spectroscopic methods, determines bioavailability and environmental risk. The exchangeable and carbonate-bound fractions represent the most hazardous pools. Remediation strategies include established physical methods like soil washing, encapsulation, electrokinetic remediation and biological approaches such as biochar amendment, phytoremediation, and organic immobilization agents. Combined approaches, particularly phytoremediation coupled with biochar and microbial consortia, offer an effective balance of cost-effectiveness, sustainability, and long-term efficacy. This review provides a framework for integrated, site-specific soil management grounded in scientific evidence.

Keywords: Heavy Metals; Soil Contamination; Source Apportionment; Metal Speciation; Remediation; Biochar

1. Introduction

Soil is a finite and non-renewable resource that forms the foundation of terrestrial ecosystems and global food production. Rapid industrialization, urbanization, and intensification of agricultural practices over the past century have led to widespread contamination of agricultural soils by heavy metals. These elements have atomic densities exceeding 4 to 5 g cm^{-3} and include cadmium (Cd), lead (Pb), arsenic (As), mercury (Hg), chromium (Cr), copper (Cu), zinc (Zn), and nickel (Ni) [1,2]. Unlike organic pollutants, heavy metals are non-biodegradable and persist in the soil environment for decades to centuries. They continuously pose risks to crop quality, groundwater resources, and human health through food chain transfer [2,3]. For instance, prolonged exposure to cadmium through contaminated rice has been directly linked to severe health conditions like Itai-Itai disease, while lead accumulation impairs neurological development in children.

Globally, an estimated 20 million hectares of agricultural land are contaminated with heavy metals across more than 5 million sites, with economic losses exceeding US$10 billion annually [3]. Similar challenges exist across Europe, the United States, Australia, and increasingly in developing countries across Asia, Africa, and South America [3,4]. Regulatory bodies such as the World Health Organization (WHO) and the Food and Agriculture Organization (FAO) have established strict permissible limits for these metals, yet agricultural topsoils frequently exceed these thresholds.

Understanding the sources of heavy metals is the primary step toward effective management. The speciation of heavy metals, which refers to their chemical forms and associations with soil components, is more informative for risk

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assessment than total metal concentrations. Speciation determines bioavailability, mobility, and toxicity [1,5]. Finally, a diverse array of remediation strategies has been developed, ranging from physical containment and chemical stabilization to biological approaches [2,3,6]. This review provides an evidence-based summary of the sources, speciation, and remediation strategies for heavy metal contamination in agricultural soils, with emphasis on integrated approaches that balance environmental sustainability, cost-effectiveness, and long-term efficacy.

2. Materials and Methods

This review evaluated peer-reviewed literature published between 2000 and 2025 from PubMed, Scopus, and Web of Science. Search terms included 'heavy metals', 'agricultural soil', 'contamination', 'source apportionment', 'speciation', 'remediation', 'biochar', and 'phytoremediation'. Priority was given to quantitative source apportionment studies, sequential extraction protocols, and field-scale remediation trials. Articles were screened for relevance, and data regarding heavy metal concentrations, speciation methods, and remediation efficiencies were extracted and organized into logical themes for discussion.

3. Results and Discussion

3.1. Sources of Heavy Metals in Agricultural Soils

Heavy metals enter agricultural soils through natural (geogenic) and anthropogenic pathways. While natural background levels derive from parent material weathering and are generally low, anthropogenic inputs have dramatically elevated metal concentrations in agricultural top soils worldwide [1,4]. Natural sources include the weathering of parent rock materials. Different rock types contain characteristic metal assemblages. Basaltic igneous rocks are rich in Cu, Cd, Ni, and Co, shales contain elevated Pb, Cu, Zn, and Cd, and limestone-derived soils typically have lower metal contents [4]. Atmospheric deposition from volcanic eruptions, forest fires, and wind-blown dust also contributes to background levels.

Anthropogenic sources dominate the influx of these pollutants. Source apportionment studies using Positive Matrix Factorization (PMF), UNMIX, and Principal Component Analysis have demonstrated that human activities contribute 65 to 86% of total heavy metal inputs [7,8]. Agricultural practices are a major contributor. Phosphate fertilizers are a significant source of Cd, As, and Pb, as phosphate rock contains these metals as impurities [4]. Long-term application of phosphate fertilizers leads to Cd accumulation at an annual rate of approximately 0.15% above background levels [4]. Copper-based fungicides result in significant Cu accumulation in vineyard soils. Livestock manures, particularly from intensive pig and poultry operations, contain elevated Cu, Zn, and as due to their use as feed additives for growth promotion and disease control [4,9].

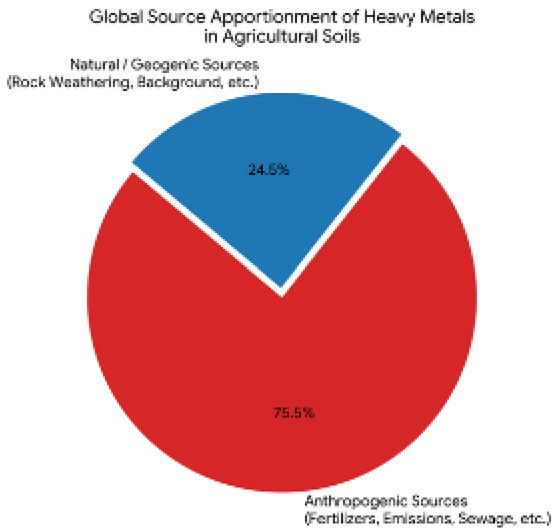

Figure 1 Average global source apportionment of heavy metals in agricultural soils, demonstrating the dominance of anthropogenic inputs (estimated range: 65 to 86%)

Atmospheric deposition from industrial emissions, coal combustion, and vehicular exhaust releases heavy metals (particularly Hg, Pb, Cd, and As) that are subsequently deposited onto agricultural land. Atmospheric deposition accounts for 25 to 85% of total heavy metal inputs across different regions, making it the dominant pathway for Pb and Hg in many areas [7,8]. Mining and smelting activities generate large volumes of metal-rich waste materials that contaminate surrounding agricultural soils through wind dispersion, runoff, and acid mine drainage [3]. Irrigation with wastewater or water from rivers receiving industrial and urban effluents is also a significant vector for metal entry, particularly in arid and semi-arid regions [1].

Table 1 Common sources and typical characteristics of heavy metals in agricultural soils

Heavy Metal	Primary Anthropogenic Sources	Mobility in Soil
Cadmium (Cd)	Phosphate fertilizers, smelting, sewage sludge	High
Lead (Pb)	Vehicle emissions, battery manufacturing, paints	Low
Arsenic (As)	Pesticides, mining runoff, coal combustion	Moderate to High
Copper (Cu)	Fungicides, pig/poultry manure, electroplating	Moderate
Zinc (Zn)	Manure, galvanized products, fertilizers	Moderate

3.2. Speciation of Heavy Metals in Agricultural Soils

The total concentration of a heavy metal in soil is a poor predictor of environmental risk. The chemical form or speciation determines metal mobility, bioavailability, and toxicity [1,5,10]. Operational fractionation using sequential extraction procedures partitions total metal content into defined fractions based on solubility. The Tessier procedure (five fractions: exchangeable, carbonate-bound, Fe-Mn oxide-bound, organic-bound, and residual) and the BCR procedure (four fractions: weak acid-soluble, reducible, oxidizable, and residual) are the most widely used methods [5,10]. The exchangeable and carbonate-bound fractions are considered the most bioavailable and pose the greatest immediate risk, while the residual fraction, trapped within mineral crystal lattices, is largely unavailable under natural conditions [1,5].

Three master variables control metal speciation. Soil pH is the single most important factor. Metal solubility decreases by approximately 100-fold per unit pH increase for cationic metals such as Cd^{2+} and Pb^{2+} [1]. Soil organic matter contains carboxyl, phenolic, and thiol functional groups that form stable complexes with metal ions. The affinity sequence follows $Cu^{2+} > Hg^{2+} > Cd^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+}$ [4,9]. Redox potential (Eh) also plays a critical role. Reducing conditions in waterlogged paddy soils promote Fe- and Mn-oxide dissolution, releasing associated metals. Under strongly reducing conditions, sulfate reduction produces sulfide (S^{2-}), which precipitates metals as highly insoluble sulfides [1].

Advanced analytical methods provide molecular-scale information beyond operationally defined fractions. X-ray absorption fine structure (XAFS) spectroscopy identifies oxidation states and local coordination environments of metals in soil matrices without disrupting sample integrity [10]. Synchrotron-based μ-XRF and NanoSIMS provide spatially resolved elemental distribution maps at micrometer to sub-micrometer scales. Diffusive gradients in thin films (DGT) measure the kinetically labile metal pool most relevant for plant uptake by simulating root-induced metal mobilization [11]. For tropical soils prevalent in countries like Nigeria and Brazil, standard sequential extraction procedures require modification. Silveira et al. [5] developed a modified procedure that includes separate steps for Mn oxides, amorphous Fe oxides, and crystalline Fe oxides, providing more accurate speciation data for highly weathered tropical soils.

Table 2 Sequential extraction fractions (Tessier method) and their environmental significance

Soil Fraction	Extraction Condition	Bioavailability / Significance
Exchangeable	Neutral salts (e.g., MgCl2)	Highly bioavailable; direct risk to plants
Carbonate-bound	Mild acids (e.g., Sodium acetate)	Susceptible to changes in soil pH
Fe-Mn Oxide-bound	Reducing agents (e.g., Hydroxylamine)	Released under reducing, waterlogged conditions
Organic-bound	Oxidizing agents (e.g., H2O2 / HNO3)	Released during organic matter degradation
Residual	Strong acid digestion (e.g., HF / HClO4)	Non-bioavailable; held within crystal lattices

3.3. Remediation Strategies

Remediation technologies for heavy metal-contaminated soils fall into three broad categories: physical, chemical, and biological methods [2,3,6]. No single remediation method is universally optimal. The most effective and sustainable strategies increasingly adopt an integrated approach that combines multiple technologies tailored to site-specific conditions [3,6].

3.3.1. Physical Methods

Soil replacement and capping involve excavating contaminated soil and replacing it with clean soil, or capping with impermeable materials such as asphalt, concrete, or clay liners. This is effective for small, heavily contaminated sites but is expensive ($270 to $460 per ton), labor-intensive, and transfers contamination rather than eliminating it [2]. Soil washing uses chemical solutions (acids, chelating agents such as EDTA, surfactants) to extract metals from the soil matrix. It is effective for coarse-textured soils but can damage soil structure, reduce fertility, and generate hazardous wastewater requiring further treatment. Costs range from $70 to $183 per m^3 [3]. Electrokinetic remediation applies an electric field across contaminated soil, causing metal ions to migrate toward electrodes by electromigration and electroosmosis. This technique is particularly effective for fine-grained, low-permeability soils where other methods are less applicable. However, soil pH fluctuations near the electrodes can limit efficiency, and treatment times can be prolonged. Costs range from $25 to $295 per m^3 [3,6].

3.3.2. Chemical Methods

Immobilization and stabilization reduce metal mobility and bioavailability by adding amendments that induce precipitation, adsorption, or complexation. Common amendments include liming materials ($CaCO_3$, CaO) which increase soil pH and promote metal hydroxide precipitation. Phosphates (apatite, rock phosphate, bone meal) form highly insoluble metal-phosphate precipitates such as pyromorphite for Pb. Clay minerals (zeolite, bentonite, montmorillonite) immobilize metals through cation exchange and surface adsorption. Metal oxides (Fe, Mn, Al oxides) provide high-surface-area sorption sites [2,6]. Immobilization is cost-effective ($20 to $520 per m^3) and suitable for large areas, but metals remain in the soil and may be remobilized under changing environmental conditions [6].

Biochar amendment has emerged as an excellent amendment for heavy metal immobilization. Biochar is a carbon-rich material produced by pyrolysis of biomass under oxygen-limited conditions. It immobilizes metals through multiple mechanisms. Its alkalinity increases soil pH (liming effect), reducing metal solubility. Oxygen-containing functional groups (carboxyl, hydroxyl, phenolic) bind metal cations through surface complexation. Its high cation exchange capacity promotes ion exchange with metal cations. Mineral components (carbonates, phosphates) form insoluble metal precipitates, and its porous structure provides abundant physical sorption sites [11,12]. However, challenges remain, including variable biochar characteristics depending on feedstock and pyrolysis conditions, potential release of toxic substances from contaminated feedstocks, possible activation of certain metals such as As at elevated pH, and the need for standardized application protocols [11].

Organic amendments (compost, manure, crop straw, sewage sludge) improve soil properties while immobilizing heavy metals through complexation with humic substances, microbial-mediated reduction, and co-precipitation with soil minerals [9]. The mechanisms include electrostatic adsorption, specific complexation with functional groups, reduction of high-valence metals (e.g., Cr^{6+} to Cr^{3+}), and formation of organo-mineral co-precipitates [9]. These amendments also enhance soil fertility, microbial diversity, and plant growth, making them particularly suitable for agricultural contexts.

3.3.3. Biological Methods

Phytoremediation uses plants to extract, stabilize, or volatilize heavy metals from soil. It is an environmentally friendly and cost-effective remediation approach, costing approximately ten times less than physical or chemical methods [2,6,13]. Three main mechanisms are recognized. Phytoextraction involves hyperaccumulator plants (e.g., Brassica juncea, Tulasi caerulescens, Sedum Alfredia, Pteris vittata for As) that absorb metals through roots and translocate them to above-ground biomass, which is then harvested and disposed of [13]. Approximately 400 hyperaccumulator plant species have been identified, belonging primarily to the Brassicaceae, Asteraceae, Fabaceae, and Poaceae families. Phyto stabilization involves plants immobilizing metals in the rhizosphere through root exudates, microbial symbioses, and physical stabilization of soil. Phytovolatilization involves plants taking up metals and releasing them as volatile compounds (primarily Hg and Se) to the atmosphere [13].

The main limitation of phytoremediation is the extended time required, particularly for deep or heavily contaminated soils. However, the combination of phytoremediation with biochar, organic amendments, and plant growth-promoting rhizobacteria (PGPR) has been shown to significantly enhance remediation efficiency [13]. Microbial remediation employs bacteria (e.g., Bacillus, Pseudomonas, Beobachter), fungi (e.g., Aspergillus, Phanerites chrysophobia), and algae to immobilize heavy metals through biosorption (passive binding of metals to cell wall functional groups such as carboxyl, phosphate, and hydroxyl), bioaccumulation (active intracellular uptake), biomineralization (microbial-induced precipitation of metal carbonates, phosphates, or sulfides), and redox transformation (reduction of Cr^{6+} to Cr^{3+}, Hg^{2+} to Hg^{0}, or As^{5+} to As^{3+}) [2,9].

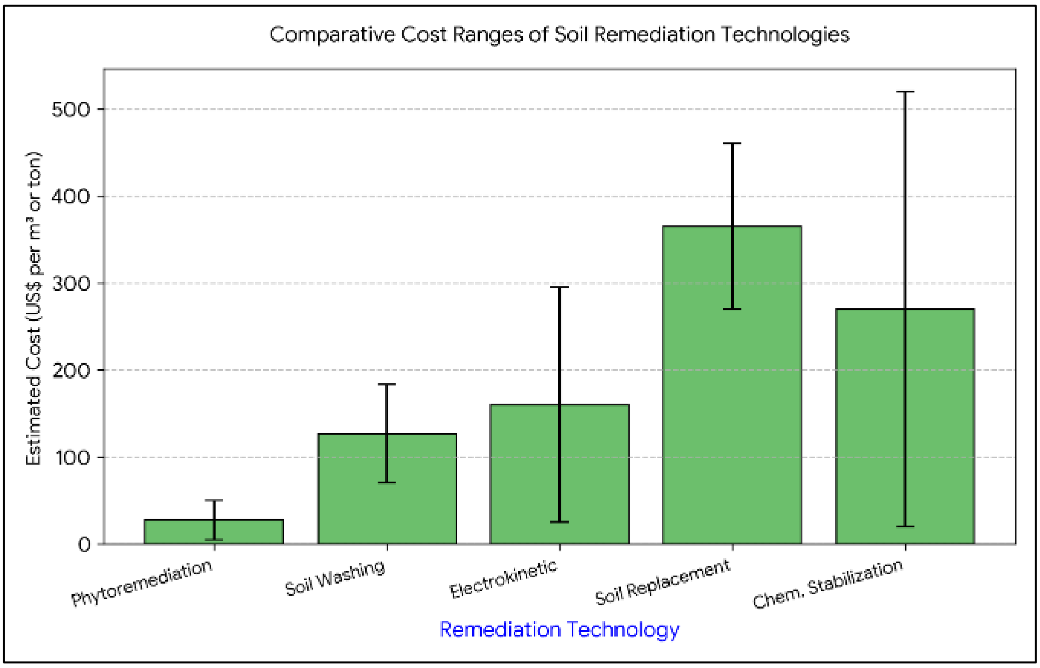

Figure 2 Estimated cost ranges (US$) for various heavy metal soil remediation technologies, highlighting the cost-effectiveness of phytoremediation

Table 3 Overview of selected remediation technologies for heavy metal-contaminated soils

Remediation Type	Specific Approach	Primary Mechanism
Physical	Soil Washing	Extraction using acids or chelating agents
Physical	Electrokinetic	Electromigration of ions via electric field
Chemical	Chemical Stabilization	Precipitation or adsorption using liming/clay
Chemical	Biochar Amendment	Surface complexation and pH alteration
Biological	Phytoextraction	Uptake and translocation into plant shoots
Biological	Microbial Remediation	Biosorption, biomineralization, redox change

3.4. Knowledge Gaps and Future Directions

Despite substantial progress, several knowledge gaps remain. Long-term field studies (5 to 10 years or more) are urgently needed to assess the durability and sustainability of immobilization treatments under realistic environmental conditions, as most current studies are laboratory-scale or short-term pot experiments [3,11]. Standardization of biochar protocols for feedstock selection, pyrolysis conditions, quality control, and application rates is required to ensure reproducibility [11]. Real-time monitoring of metal speciation during flooding-drying cycles, seasonal temperature changes, and aging processes is essential for predicting long-term risk [10]. The complex interactions between remediation amendments, soil microbial communities, and metal speciation remain poorly understood. Metagenomic and meta transcriptomic approaches can elucidate the functional roles of key microbial taxa [9]. Finally, the use of waste materials for remediation aligns with circular economy principles but requires rigorous assessment of potential secondary contamination risks [3].

4. Conclusion

Heavy metal contamination of agricultural soils is a complex challenge requiring integrated scientific and management approaches. This review has demonstrated that anthropogenic activities, particularly fertilizer use, atmospheric deposition, industrial emissions, and sewage irrigation, are the dominant contributors, accounting for 65 to 86% of total heavy metal inputs. The environmental risk of heavy metals is governed by their chemical form, not total concentration. Therefore, sequential extraction and advanced spectroscopic methods are essential tools for assessing bioavailability and guiding remediation decisions. A diverse portfolio of remediation technologies is available, with biochar amendment, phytoremediation, and organic immobilization agents representing the most environmentally sustainable and cost-effective strategies for agricultural soils, particularly when applied in integrated combinations. Priority areas for future research include long-term field validation, standardization of amendment protocols, dynamic speciation monitoring, microbial community engineering, and circular economy-based approaches. Effective management of heavy metal-contaminated agricultural soils is essential for food security, environmental protection, and human health.

Compliance with ethical standards

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Disclosure of conflict of interest

No conflict of interest to be disclosed.

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