

Advancement of metal(loid) research on farmland

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KEYWORDS

Metal(loid) pollution, metal(loid) remediation, metal(loid) sources, soil

HIGHLIGHTS

- It is crucial to comprehensively summarize remediation technologies and identify future development directions.
- This review systematically summarizes various soil remediation and improvement technologies, incorporating multiple disciplines including physics, chemistry and biology, as well as their interdisciplinary intersections.
- A solid foundation is given for the healthy development of soil.

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GRAPHICAL ABSTRACT



ABSTRACT

Metal(loid) pollution has emerged as a pressing environmental issue in agriculture, garnering extensive public attention. Metal(loid)s are potentially toxic substances that infiltrate the soil through diverse pathways, leading to food chain contamination via plant uptake and subsequent animal exposure. This poses a serious threat to environmental quality, food security, and human health. Hence, the remediation of metal(loid)-contaminated agricultural soil is an urgent concern demanding immediate attention. Presently, the majority of research papers concentrate on established, isolated remediation

technologies, often overlooking comprehensive field management approaches. It is imperative to provide a comprehensive summary of remediation technologies and identify future development directions. This review aims to comprehensively summarize a range of soil remediation and enhancement technologies, incorporating insights from multiple disciplines including physics, chemistry, biology, and their interdisciplinary intersections. The review examines the mechanisms of action, suitable scenarios, advantages, disadvantages, and benefits associated with each remediation technology. Particularly relevant is the examination of metal(loid) sources, as well as the mechanisms behind both established and innovative, efficient remediation and enhancement technologies. Additionally, the future evolution of remediation technologies are considered with the aim of offering a scientific research foundation and inspiration to fellow researchers. This is intended to facilitate the advancement of remediation technologies and establish a robust foundation for sustainable development of soil.

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1 Sources of metal(loid)

Metal(loid) presented in agricultural soil poses a direct threat to both food safety and the ecological environment. Soil metal(loid) can pose a risk to the entire food chain by being absorbed by plants and subsequently entering the animal food web. Also, metal(loid) pollution can detrimentally impact soil physicochemical properties, soil microbial communities, and overall soil characteristics and functions, leading to a significant decline in yield quality^[1]. Consequently, analyzing the sources of metal(loid) should prove advantageous in preventing and implementing targeted remediation of metal(loid)-contaminated soils^[2-5]. Therefore, analyzing the sources of metal(loid) is advantageous for preventing and remedying contaminated soils^[6].

The introduction of metal(loid) into agroecosystems primarily occurs through a combination of natural processes and human activities^[7]. A view held by many scholars is that the contributions of natural sources of metal(loid) to environmental contamination are significantly overshadowed by the pollution caused by human activities. It is important to note that certain soils innately have metal(loid) from their geological origins, constituting natural sources of metal(loid) that can have adverse effects on plants and organisms^[8]. Metal(loid) from rocks can infiltrate the soil environment via natural mechanisms such as atmospheric deposition, biological activity, terrestrial processes, and volcanic activity. This infiltration may also occur through corrosive leaching and surface winds. Anthropogenic activities disrupt the naturally occurring, gradual geochemical cycles of metal(loid), resulting in the accumulation of one or more metal(loid) in the soil.

Recent advancements in the agricultural sector, industrialization, and urbanization have played a significant role in the escalating contamination of soils with metal(loid)^[9]. Human activities, including mining and smelting, fossil fuel combustion in refineries, municipal waste disposal, pesticide application, sewage irrigation and fertilizer usage, have elevated metal(loid) concentrations in the agricultural soil environment^[10]. Excessive use of agricultural inputs such as pesticides, fertilizers, mulch, livestock manure and sludge-based compost products can result in metal(loid) contamination of farmland. Certain pesticides contain metal(loid) that can enter the soil during seed disinfection and pesticide spraying processes^[11]. Although pesticides containing As, Hg, and Pb have been prohibited in the majority of countries, fungicides containing Cu and Zn remain extensively used in global agricultural production^[12] (Fig. 1).

Currently, agriculture continues to rely heavily on pesticide application, as pesticides are inseparable from modern agriculture. To sustain agricultural production, the complete elimination of pesticides is not currently feasible. Consequently, it is imperative to address the annual influx of metal(loid) into farmland through pesticides, which can lead to direct soil metal(loid) contamination. In contemporary agricultural practices, the intensified use of fertilizers is key for achieving high yields. Notably, metal(loid) represents the most commonly reported contaminants in fertilizers, with metal(loid) mass fractions typically in the order: phosphate fertilizers > compound fertilizers > potash fertilizers > nitrogen fertilizers. Apart from metal(loid) presented in mineral fertilizers, particularly phosphorus-based fertilizers, the

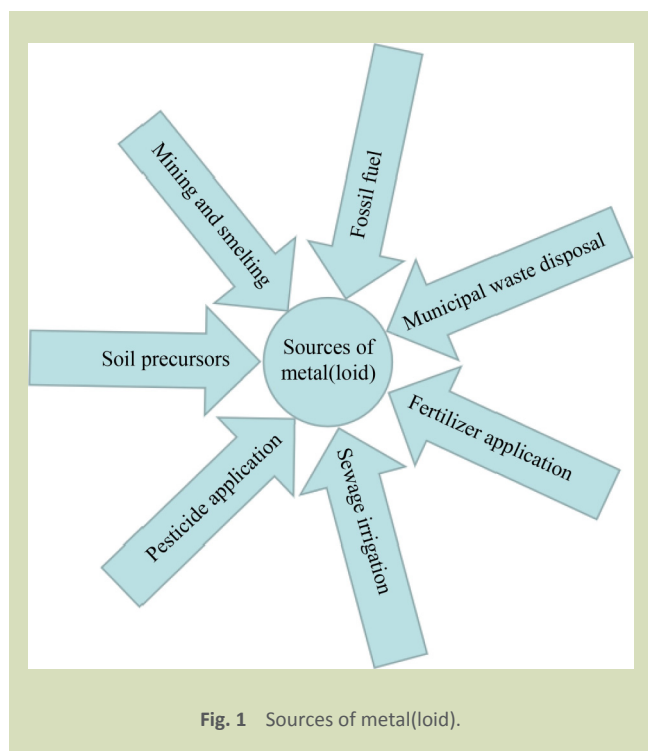


Fig. 1 Sources of metal(loid).

growing use of waste fertilizers and sludge-based fertilizers has emerged as significant contributors to soil metal(loid) contamination. The soil environment has limited capacity to accommodate metal(loid) elements, and their rapid enrichment and subsequent pollution of the soil are exacerbated by imprudent fertilization practices, including excessive usage and shortened cycles. Simultaneously, the excessive application of fertilizers leads to soil acidification, amplifying the toxic effects due to heightened activity of metal(loid) ions in acidic soil conditions.

The use of agricultural mulch, which incorporates Cd and Pb heat stabilizers introduced during production, further elevates the potential for metal(loid) contamination in agricultural soils. Agricultural mulch is extensively used in agricultural production due to its durability and stability. Heat-stable salts of metal(loid) elements such as Zn, Cd, Sn, Ba, and Pb are incorporated as heat stabilizers during the mulch manufacturing process. Agricultural mulch, when applied to cover crop surfaces, is subject to prolonged exposure to natural environmental conditions. Over time, the mulch ages and deteriorates due to the effects of sunlight, wind and rain. Following crop harvesting, the remnants of broken mulch persist in the field soil. Due to its limited capacity for degradation, the accumulated mulch increasingly becomes a source of soil metal(loid) contamination as its quantity and age increase. This situation poses a substantial risk to both

agricultural production safety and ecological health.

The persistent use of livestock manure and its composted products has increasingly exacerbated metal(loid) pollution in farmland. During livestock farming, apart from the use of feed additives containing Cu and Zn, there are instances where additives containing As, Cd, Cr, Pb, and Hg are used. The mass fractions of As, Cr, Cu, Pb, and Zn in the soil profiles of agricultural fields with prolonged livestock manure application surpass those of the control group, with Cu and Zn exceeding the control group significantly. As, Cr, Cu, Pb, and Zn in municipal sludge are particularly prone to surpassing control standards, and their application can lead to varying degrees of increased mass fractions of metal(loid) in agricultural soils^[13]. Metal(loid)s presented in solid waste have high mobility and disperse into the surrounding soil and water bodies in a radial and porous manner. These metal(loid) ions have the potential to induce severe pollution of both soil and groundwater.

Environmental alterations in groundwater due to mining industry activities have led to shifts in the chemical composition of groundwater, and the infiltration of tailings and other waste materials, resulting in profound groundwater contamination. Research has demonstrated that metal(loid) concentrations in the soil within landfill and waste collection areas consistently exceed established safety thresholds^[14]. Electronic devices and their waste materials contain significant quantities of Cu, Zn, Cr, Hg, Cd, Pb, and others. The processes of dismantling, recycling, and disposal can result in metal(loid) pollution, with inadequate treatment potentially causing soil contamination that exceeds metal(loid) standards and may even extend to the surrounding environment. Such contamination poses a substantial threat to crop safety and public health.

The deposition of pollutants from the atmosphere is a crucial contributor to metal(loid) contamination in soil. Anthropogenic sources of metal(loid) in the atmosphere include fuel combustion, industrial production, transportation, mining metallurgy, and soil dust^[15]. Also, factors influencing the atmospheric deposition of metal(loid) include population density, long-distance transport from remote sources, waste incineration, and straw burning. Pb, Zn, and Cu primarily originate from coal-fired fuel, industrial production, vehicular wear and tear, and exhaust emissions. Cr and Ni mainly result from coal combustion, while Hg pollution primarily emanates from fuel combustion, mining and waste incineration. The deposition of metal(loid) pollutants on plant surfaces primarily occurs through two mechanisms: (1) deposition onto the plant

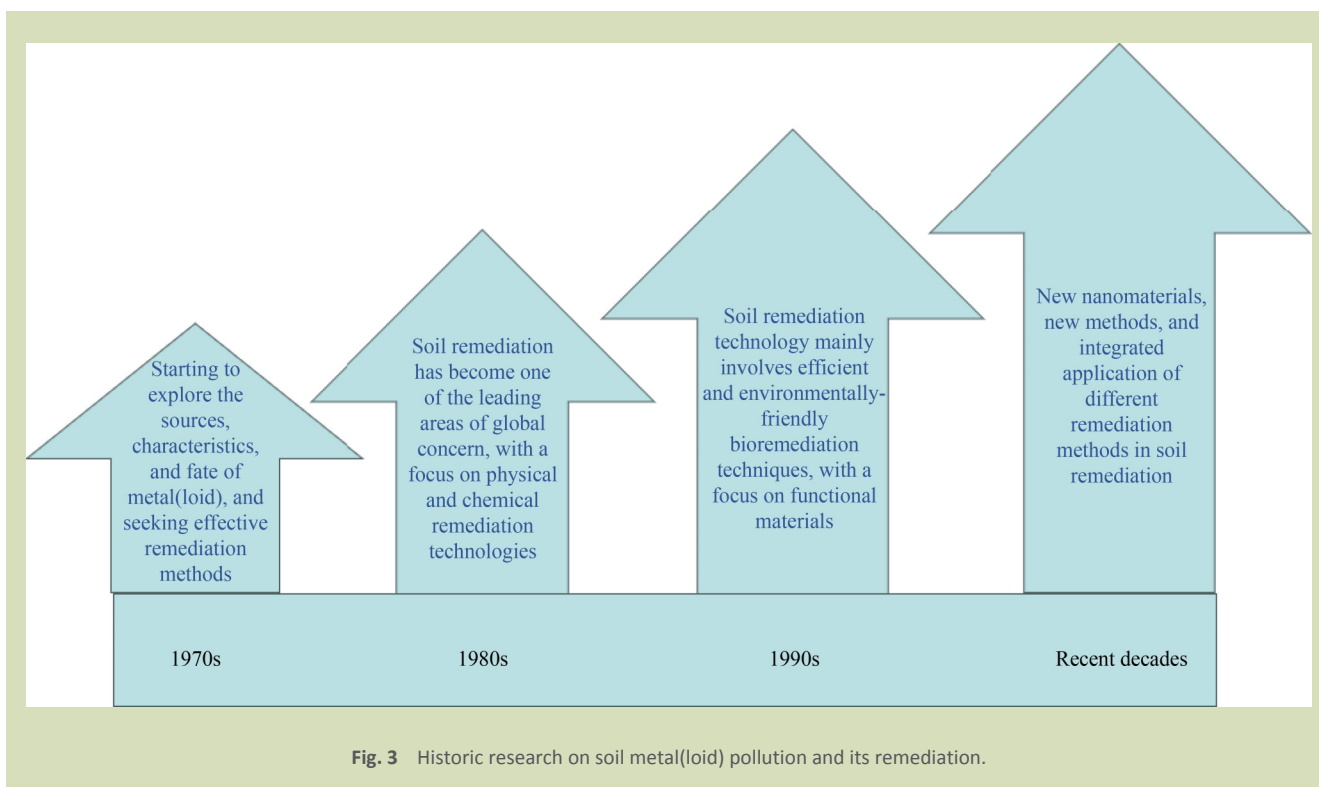


Fig. 3 Historic research on soil metal(loid) pollution and its remediation.

The paper examines the principles, application conditions, advantages, disadvantages, and technical feasibility of these remediation techniques (Table 1). Additionally, this paper explores natural attenuation, an earth science-based

remediation strategy for soils contaminated with metal(loid)^[20]. Lastly, the paper offers recommendations for the selection of suitable remediation technologies, addressing crucial knowledge gaps, and tackling practical challenges.

Table 1 Established metal(loid) remediation technology

Technique	Classification	Application	Advantages	Disadvantage
Physical remediation	Guest soil mulching	Lightly contaminated soils	Thoroughness	High investment costs
	Surface stripping	Heavily contaminated areas	Stability	May damage the soil structure
	Deep plowing			Cause soil fertility decline
	Dilution			Change out of the dirty soil to pile or disposal
	Soil replacement			
	Isolation			
	Heat treatment			
Chemical remediation	Drenching			
	Curing/stabilization	Lightly contaminated soils	Reducing metal (loid) migration	High investment costs
	Vitrification	Heavily contaminated areas	Changing the properties of metal(loid)	Does not remove Metal(loid) completely from the soil
	Soil drenching			
Microbial remediation	Electroremediation			
	Adsorption by microbial	Lightly contaminated soils	Low-cost	Greatly influenced by environmental factors, pollutant properties and concentrations, local climatic conditions, site hydrogeological conditions
	Precipitation by microbial	Heavily contaminated areas	Environmentally-friendly	Cause greater potential harm
	Leaching by microbial		Economic benefits	Application is still difficult
	Transformation by microbial		Ecological sustainability	
Phytoremediation	Volatilization by microbial			
	Phytoextraction	Lightly contaminated soils	Green and environmentally-friendly	Efficiency
	Phytofiltration	Heavily contaminated areas		Community balance
	Phytostabilization			
	Phytovolatilization			
	phytodegradation			

2.1 Physical remediation techniques

Physical remediation techniques encompass practices such as soil mulching with clean soil, surface stripping, deep plowing and dilution, soil replacement, isolation, heat treatment, and drenching. These methods offer a straightforward, rapid, and reasonably stable approach to soil remediation. Soil replacement, deep plowing and soil mixing with uncontaminated soil are effective strategies for decreasing metal(loid) content in soil and mitigating their harmful impacts on the soil-plant system. These measures facilitate compliance with food hygiene standards for agricultural products. Deep tillage is suitable for lightly contaminated soils, while the use of earth addition or exchange is more suited to heavily polluted contexts^[21].

Prior to soil mulching, an impermeable clay layer is established. The mulch thickness typically ranges from 20 to 40 cm, contingent upon soil characteristics, mulching approach, and environmental conditions. Post-remediation, ongoing monitoring of cultivation is imperative. Nevertheless, this technology involves high engineering demands and costs. Procuring the clean soil needed for adding soil is often a challenging task, and such soil typically has low fertility. Also, variations in soil texture between batches make achieving uniform mixing difficult, leading to divergent physical and chemical properties and reduced fertility in context where soil has been added to fields.

Methods like soil surface cover, landfill, and encapsulation prove effective in decreasing the diffusion potential of pollutants. They curtail the movement of contaminants within the soil and the food chain, enhancing the sustainable use of soil. A common method to hinder the diffusion of metal(loid) is the installation of containment walls^[22]. The use of impermeable materials intercepts metal(loid) in all directions. Although isolation walls do not directly remediate contaminants, they can substantially curtail the migration of metal(loid) into groundwater.

Thermal treatment is the heating of soil for remediation purposes, exploiting the volatility of contaminants. Standard heating techniques use conductive heating, resistance heating, and other methods. Heating has been demonstrated to effectively eliminate pollutants with high vapor pressure. However, it is essential to recognize that heating can impact the physical, chemical, and biological aspects of soil health. Thermal treatment uses high-frequency voltage to generate electromagnetic waves, producing heat energy that heats the soil. This process desorbs contaminants from the soil particles

and expedites the separation of certain volatile metal(loid) from the soil, all for the purpose of remediation.

Physical approaches are the original methods for addressing soil metal(loid) pollution. These methods offer the benefits of comprehensiveness and stability. However, their extensive engineering and substantial costs can potentially harm soil structure, decrease soil fertility, and necessitate the disposal or containment of contaminated soil.

2.2 Chemical remediation techniques

Chemical remediation is a technique that uses chemical reagents, reactions, and principles to eliminate contaminants. The primary remediation methods encompass curing/stabilization, vitrification, soil drenching, and electroremediation. Solidification/stabilization technology involves the uniform blending of solidified/stabilized materials into the soil, thereby curbing the migration of metal(loid) through interactions between these materials and metal(loid)^[23].

Curing involves the physical encapsulation of contaminants within a solid matrix generated from materials such as cement, asphalt, bitumen, and thermoplastic binders. Simultaneously, stabilization involves chemical reactions aimed at decreasing the mobility of contaminants and modifying specific physicochemical properties of the soil, and more soil pH, redox potential. In this approach, one or more passivating materials are introduced to the contaminated soil. This addition serves to decrease the uptake of metal(loid) by crops by altering soil physicochemical properties and facilitating a range of reactions, including precipitation, adsorption, complexation, and oxidation-reduction. These transformations modify the morphology of metal(loid) in the soil and decrease their biological impact. However, it is important to note that this remediation method alters the presence of metal(loid) in their existing form in the soil but does not eliminate them from the soil.

Vitrification, also known as molten glass treatment, is a curing and stabilization method that involves the application of high thermal energy (ranging from 1400 to 2000 °C). This process involves blending contaminated soil with glass-forming precursors, subjecting the mixture to intense heat until it liquefies, and ultimately yielding an amorphous homogeneous glass matrix upon cooling. Within the glass matrix, metal(loid) can be immobilized through two primary interactions: chemical bonding and encapsulation. These interactions form

the basis for the effective decontamination of metal(loid)-contaminated soil.

Soil drenching is an effective remediation technique for extracting contaminants from soil through the application of water or suitable rinsing solutions. To achieve optimal removal of metal(loid), the use of detergents such as water, saponin, organic acids, chelating agents, surfactants, and low-molecular-weight organic acids has been found to effectively facilitate the desorption of contaminants from the soil. This method endeavors to eliminate metal(loid) from contaminated soil matrices through various mechanisms, including electromigration, electroosmosis, electrophoresis, and electrolysis.

Electroremediation involves the application of a direct current voltage to both sides of the contaminated soil, creating an electric field gradient. This electric field induces the movement of metal(loid) ions within the soil toward the opposing electrodes. This migration occurs through mechanisms such as electromigration (movement of ions in the soil solution toward oppositely charged electrodes), electroosmotic flow (movement of the soil solution relative to charged soil particles under the influence of the electric field, typically from the anode to the cathode) or electrophoresis (motion of charged colloidal particles within the soil solution under the influence of the electric field)^[24]. These processes drive the metal(loid) ions toward the respective electrode poles, leading to the decontamination of the soil^[25].

Chelating agents are used to enhance the effectiveness of electroremediation in contaminated soils. Researchers have explored the mobility of various metal(loid) (including As, Cd, Cr, Cu, Ni, Pb, and Zn) by assessing the impact of different chelating agents (such as EDTA, and ethylenediamine-succinic, nitrotriactic, and citric acids) on the efficiency of electroremediation. Also, some researchers have integrated drenching and electrokinetic remediation in a complementary manner to overcome the limitations of rinsing techniques in soil remediation. Researchers observed that the incorporation of pumps in electrokinetic drenching remediation led to enhanced removal efficiency for Co^{2+} and Cs^+ from contaminated soils.

2.3 Microbial remediation techniques

Microbial remediation is one of the more recent approaches for partially remediating metal(loid)-contaminated soil ecosystems. This technique harnesses the intrinsic biological mechanisms of microorganisms to eliminate, break down, or

immobilize detrimental contaminants within the polluted environment. Microorganisms primarily remediate metal(loid)-contaminated soils through mechanisms including adsorption, precipitation, leaching, transformation, and volatilization^[26]. The efficiency of metal(loid) remediation depends on a range of factors, including redox processes, cellular metabolic activity, methylation, and intracellular accumulation and secretion. It also involves metabolism-independent mechanisms, characterized by passive uptake processes mediated by cell wall components, proteins, extracellular polysaccharides, and bacterial iron carriers. Various factors impact this efficiency, including the properties and concentrations of pollutants, local climatic conditions, site hydrogeological conditions, and the specific bioremediation technology used.

Bioremediation is a particularly economical and environmentally-friendly approach to soil metal(loid) remediation. In contrast to alternative methods, bioremediation adopts a natural approach to remediate soil, offering superior economic and ecological sustainability. Metal(loid) bioremediation can be accomplished through the use of microorganisms, plants, or a combination of both^[27]. Bacteria and fungi are frequently used for the remediation of metal(loid)-contaminated soil, alongside the use of algae and yeast. The collective remediation involving multiple bacterial communities typically yields enhanced efficiency. Microorganisms possess the capacity to modify metal(loid) and modify their oxidation states. In redox processes, microorganisms proficiently modify the speciation of metal(loid) within the soil environment through their metabolic activities, thereby influencing their activity and toxicity. This often results in increased volatility and water solubility^[28]. Consequently, microorganisms can decrease the bioavailability of metal(loid) through precipitation and bioleaching. Microorganisms have been found to have specific genes associated with drug resistance. Microbial cell walls serve as effective sites for the adsorption of metal(loid). Their mechanism of action is rooted in the composition of the cell wall, encompassing a complex array of functional groups (including mercaptan, thioether, sulfonate, phosphine, thiol, hydroxyl, ester, amine, and carboxyl). These groups facilitate interactions between various metal(loid) ions and the cell wall through electrostatic forces, hydrogen bonding, and other modes of interaction. The presence of extracellular polymers significantly influences metal adsorption and the acid-base properties of microorganisms, contingent on their chemical characteristics.

Environmental factors, such as humidity, temperature, pH, and

salinity, influence the efficiency of microbial cell adsorption of metal(loid). Upon contact with microbial cells, metal(loid)s activate their defensive mechanisms, such as inducing oxidative stress. This defensive response decreases the bioavailability of metal(loid)^[29]. Enzymatic processes instigated by microorganisms facilitate the conversion of mineralized and aggregated metal(loid) in the soil into a stable state as carbonates. During processes involving precipitation and dissolution, microorganisms use available soil nutrients and energy resources through their metabolic activities to generate a variety of macromolecular acids (such as citric acid and oxalic acid). These acids either chelate metal(loid) or precipitate them as oxalate compounds, thereby curtailing their mobility in the soil. Also, as part of their metabolism, microorganisms generate an array of low-molecular-weight organic acids (including formic, acetic, propionic, and butyric acids). These small molecular acids possess the capacity to directly or indirectly dissolve soil metal(loid), consequently enhancing the effectiveness of bioremediation.

Currently, microbial remediation technology remains mostly within the confines of laboratory research and poses challenges in practical application. This is largely due to the nature of microorganisms, making their collection, manual regulation, and subsequent retrieval and treatment complex tasks. Also, the metabolic activities of microorganisms are significantly impacted by environmental factors, including soil nutrient levels, temperature, and moisture. Variations in environmental conditions can introduce instability in the efficacy of remediation efforts. Additionally, microorganisms have substantial variability and have the capacity to deviate from anticipated transformation pathways of soil metal(loid) pollutants. This can result in the generation of more toxic derivatives, posing an increased risk to the soil environment.

2.4 Phytoremediation techniques

Phytoremediation techniques use plants with the explicit purpose of lowering the concentration or mitigating the toxic effects of pollutants within the environment. Phytoremediation techniques encompass a range of approaches, including phytoextraction, phytofiltration, phytostabilization, phytovolatilization, and phytodegradation. These methods involve the absorption, degradation, precipitation, chelation, and redox transformation of metal(loid) within contaminated soils, facilitated by the metabolic activities of plants. Used in combination, these can decrease the concentration and biological impact of metal(loid) in the soil^[30].

Phytoextraction involves the absorption of contaminants from

soil or water by plant roots and their subsequent translocation to shoots or other harvestable plant parts. This process serves the dual purpose of removing impurities and sustaining soil health. Filtration processes, encompassing root, shoot, and stem filtration, facilitate the sequestration of metal(loid).

Plant stabilization aims to decrease the mobility and bioavailability of contaminants within the environment. This can be achieved using specific substances secreted by plant roots or inter-roots to alter the morphology of metal(loid) in the soil, transforming them into less toxic or comparatively benign compounds. Subsequently, metal(loid)-enriched plants further reduce these substances, decreasing their activity and mobility. This process serves to safeguard against soil metal(loid) contamination, preventing their leaching into groundwater or dispersal into the atmosphere, thereby averting contamination of other environments^[31].

Plant volatilization involves the use of plants to absorb metal(loid), converting them into volatile forms that are subsequently released to the atmosphere. Plant volatilization technology relies on specific substances secreted by plant roots or inter-root microorganisms to modify the chemical composition of metal(loid) in the soil, facilitating their release into the atmosphere from the soil surface. Alternatively, plants can absorb metal(loid) from the soil and transport them to their shoot. Through a sequence of physiological and biochemical reactions, these metal(loid)s are ultimately transformed into volatile compounds and released to the atmosphere. This process serves to decrease the concentration of metal(loid) within the soil.

Plant degradation pertains to the transformation or breakdown of metal contaminants within plant metabolism following their uptake from the soil^[32]. Numerous plant species demonstrate the capacity to hyperaccumulate substantial quantities of specific metal(loid) within their aboveground tissues, devoid of any adverse effects on the plant itself.

Metal(loid) from the environment initially interact with various compounds found in cell walls, cell membranes, and vesicle membranes within the plant. This interaction renders them either non-toxic or subjects them to expulsion via multiple transporters present in the membrane. Root exudation is pivotal in regulating the entry of metal(loid) ions into plant cells and can effectively limit the mobility of metal(loid). Root exudates encompass various types classified based on their molecular weight into low and high molecular weights. The cell wall serves as the primary impediment for metal(loid) ions entering the cytoplasm. Similar to the plasma membrane, the

plant cell wall comprises an array of components, including cellulose, hemicellulose, pectin, and lignin, which have abundant negative charges. These components impede the entry of Pb^{2+} into the cell interior through processes including adsorption and precipitation^[33]. The plasma membrane surface has a robust negative charge and possesses the capacity to adsorb significant quantities of positively charged Pb^{2+} , thereby impeding Pb^{2+} uptake and transmembrane transport.

Advances in molecular biology techniques have led to the gradual discovery of crucial plasma membrane transport proteins capable of expelling Pb^{2+} from cells, thereby averting potential toxic effects on plants. In the event that substantial quantities of metal(loid) ions go untreated, they have the potential to traverse the plant cell wall and various membrane structures, gaining access to the cell interior. To counteract this phenomenon, the plant uses substances found in the cytoplasm, including glutathione, proteins, and citric acid, to engage in further chelation of excess metal(loid) ions. This process results in the formation of stable complexes that decrease the biological activity of metal(loid) ions^[34]. Nonetheless, due to their limited biomass and slow growth, most phytoaccumulators are ill-suited for practical field phytoremediation endeavors. Biotechnological strategies aimed at enhancing plant tolerance and the accumulation of toxic metals can effectively address issues of overaccumulation. Genetic engineering of plants has been successful in facilitating the removal of various metal(loid) (such as As, Hg, Cd, Pb, Cu, and Se) from soil by plants. It also enables the production of metal detoxifying chelators like metallothionein and phytochelatin.

To encourage the extensive use of research findings, it is imperative to account for the range of complexities inherent in practical situations, amalgamate theoretical, and practical approaches, and use research method suited to specific local conditions. There remains a pressing need to continue the quest and cultivation of ideal plants characterized by rapid growth, exceptional water use efficiency, and a remarkable capacity for metal(loid) remediation (including adsorption, tolerance, and hyperaccumulation). Contemporary biological cloning techniques are being harnessed to rectify soil contamination by diverse metal(loid), addressing the challenge of composite soil pollution across multiple environments, including those afflicted by soil poverty, soil drought, atmospheric drought, arid winds, and others.

2.5 Typical soil conditioner

To mitigate the bioavailability of metal(loid) in soil, researchers

have identified various strategies, with the use of soil conditioners now being a time-tested approach. Soil additives typically harness waste materials from other production processes, aligning with principles of waste use and environmental efficiency. The remediation mechanism underlying typical soil conditioner compost in addressing soil metal(loid) contamination involves elevating the soil pH, capitalizing on the complexation of organic matter with metal(loid) within the compost and facilitating the coprecipitation of phosphorus with metal(loid). Concurrently, research has been found to be essential that recognize the remediation effectiveness of soil amendments for metal(loid) is subject to numerous influencing factors. Consequently, their application should be adaptive in accordance with the specific physical and chemical attributes of the soil.

2.5.1 Gypsum and its byproducts

Gypsum and its byproducts have been endorsed by numerous researchers as additives for remediating metal(loid) contamination^[35]. Certain studies have demonstrated that the substantial presence of Ca ions in gypsum can directly bind to arsenate, simultaneously neutralizing the negative charge on soil particles. This dual effect creates favorable conditions for the adsorption of arsenate. Gypsum not only functions in the remediation of metal(loid) in soil but also serves as a reference source for plants. Additionally, several studies have highlighted the beneficial impact of gypsum, particularly desulfurization gypsum, in addressing saline-alkali soil conditions. It constitutes a holistic and sustainable enhancement of soil properties^[36]. Metal(loid) contamination often disrupts the desirable soil aggregation structure. Gypsum is useful for facilitating the formation of soil aggregates, lowering the bioavailability of metal(loid), and fostering the sustainable development of soil-crop systems^[37].

2.5.2 Phosphorus-containing remediation agents

Phosphorus-containing remediation agents serve as valuable aids in addressing metal(loid) pollution in soil. A wide array of phosphorus modifiers, encompassing both synthetic and natural materials such as apatite, hydroxyapatite, rock phosphate, phosphate, diammonium phosphate and phosphoric acid, have been found to be effective in remediating soils contaminated with metal(loid). Phosphate compounds can immobilize metal(loid) by mechanisms such as direct metal adsorption or substitution with phosphorus compounds, P anion-induced metal adsorption, and precipitation as metal(loid) phosphates. Precipitation as metal(loid)-P has been identified as a primary mechanism for immobilizing metal(loid), including Pb and Zn. In the case of anionic

metal(loid), especially As, the addition of phosphate to soils containing As has been demonstrated to enhance the leaching of As(VI) through competitive anion exchange.

2.5.3 Industrial waste byproducts

The generation of industrial waste byproducts is a normal consequence of industrial processes. Therefore, it is important to explore the use of byproducts as potentially valuable resources. Several scholars have investigated this potential in the context of remediation of metal(loid)-contaminated soil, with a particular focus on materials like sludge and slag. It is worth noting that industrial waste byproducts are generally cost-effective options for this purpose. The effectiveness of industrial waste byproducts in remediating metal(loid) is intricately linked to their composition, encompassing metal oxides, phosphates and other chemically active constituents. Also, various types of slag are routinely generated on a global scale, including blast furnace slag, calcium silicate slag, phosphate alkaline slag, and steel slag. Among these, blast furnace slag emerges as one of the most potent adsorbents for Cu, Pb, Ni, and Zn ions across diverse ionic concentrations and pH ranges. The presence of metal oxides, hydroxides, and Ca within the slag substantially contributes to its adsorption capabilities for metal(loid)^[38].

The range of industrial products mentioned above has found extensive application in the reclamation of agricultural and acid mine lands. The introduction of alkaline substances into acidic soils effectively elevates soil pH, owing to the specific metal oxides, hydroxides, and carbonate ions present in industrial byproducts. Also, since the majority of these byproducts exist in the form of sand particles, they can be integrated into soil as enhancers of its physical and chemical attributes. This process optimizes soil physical and chemical properties, and fosters the formation and stability of soil aggregates, thereby ameliorating the structure of contaminated soil. Additionally, these byproducts contain a wealth of nutrients conducive to enhancing plant nutrition and soil quality^[39].

2.6 Typical agricultural management measures

Varied water and fertilizer supplies have diverse impacts on plant growth, physiology, contaminant transport, and morphological attributes. These impacts ultimately manifest as alterations in root and canopy morphological development, geometric configuration, plant water conduction, water flow resistance, photosynthetic physiology, leaf water potential, biomass, contaminant transport, distribution, yield, and

product quality. Water stress has the potential to induce modifications in plant stomatal behavior, root system configuration, hormone secretion, and the composition of inter-root and soil microorganisms. These changes can have a substantial influence on how plants respond to metal(loid)^[40]. Additionally, water and fertilizer management have the capacity to influence the efficacy of metal(loid), either through direct interactions or by indirectly modifying soil physical, chemical, and biological properties.

2.6.1 Fertilizer management

Using P, Zn, and Si fertilizers can mitigate the uptake, transport, and accumulation of Cd in crops through antagonistic mechanisms such as P–Cd, Zn–Cd, and Si–Cd interactions^[41]. Research has indicated that application of Si can ameliorate or alleviate the toxic impact of metal(loid) on plants, leading to a reduction in metal(loid) concentration within the plant tissues^[42]. Foliar application of Si fertilizer has proven effective in inhibiting the translocation of Cd from leaves to seeds. The application of ammonium nitrogen can lower the pH of the soil surrounding the roots, thereby promoting the solubilization of soil-bound Cd^[43].

The application of organic fertilizer can stimulate the complexing of soil organic matter with metal(loid), enhancing the adsorption and sequestration capabilities of the soil. This, in turn, has implications for the mobility and biological activity of metal(loid)^[44]. Organic fertilizers not only contribute to soil improvement, enhanced crop yields, and improved agricultural product quality but also influence the distribution of pollutants within the soil^[45]. They enhance plant capacity to remediate metal(loid)-contaminated soil and improve its resistance to environmental stress associated with such contamination^[46]. Previous research has demonstrated that the abundant functional groups and expansive specific surface area in organic fertilizers facilitate the formation of organic complexes between metal(loid) pollutant ions within the soil. This enhances soil adsorption capacity and pollutant-buffering properties, ultimately reducing the uptake of metal(loid) pollutants by plants and mitigating their adverse effects on agricultural products. However, it is important to note that applying organic fertilizers to improve Cd-contaminated soils can activate Cd elements in the soil due to the decomposition of humic and organic acid fractions during the mineralization process.

Research has demonstrated that under the influence of Cd stress, lobelia plants have superior growth and enhanced photosynthetic performance when supplied with NH_4^+ rather

than NO_3^- . NH_4^+ supplementation significantly decreases Cd uptake by lobelia roots compared to NO_3^- . Likewise, the Cd concentration and Cd^{2+} transport capacity within root cell sap are markedly lower in the NH_4^+ treatment in contrast to the NO_3^- treatment. Application of a Cd-specific fluorescent probe (Leadmium™ Green AM dye) for staining revealed a reduced fluorescence intensity in the root tips and root protoplasts in the NH_4^+ treatment when compared to the NO_3^- treatment. Using the non-damage microtesting technique, it was further observed that NH_4^+ addition led to a decrease in the inward flow of Cd^{2+} within the root meristem and elongation zone as compared to the NO_3^- treatment^[47]. Additionally, NH_4^+ promoted the fixation of Cd within the root cell wall. Consequently, through a systematic examination of the impacts of soil pH, redox potential, texture, and humic acid content on the mobility and bioactivity of Cd, it is possible to ascertain an optimal range for organic fertilizer application, select appropriate mineral fertilizer types, and determine the ideal fertilizer ratios. This approach not only facilitates the remediation of Cd-contaminated soil but also enhances plant capacity to absorb water, nutrients, and pollutants. This promotes biomass growth and fosters more favorable conditions for the enrichment of pollutants by plants. Also, this approach serves as an effective means to mitigate issues such as excessive capital expenditure and secondary environmental pollution arising from the loss of nutrients and metal(loid) pollutants in standard remediation methods^[48].

2.6.2 Irrigation management

Diverse irrigation management practices have a significant influence on plant physiology, root zone activity, and plant responses to metal(loid)^[49]. Both water and fertilizer are pivotal in shaping plant physiology and affecting soil microorganisms. Soil water has the direct capacity to regulate redox potential, thereby mitigating metal(loid) pollution. Specifically, flooding management can lower redox potential while augmenting the concentration of reduced Fe and Mn cations, as well as sulfur anions within the soil. This effect serves to impede the uptake of Cd by rice plants. In real-world field conditions, the flooding treatment resulted in a reduction of Cd content in rice. In practical agricultural applications, moisture management is influenced by seasonal precipitation patterns and sources of irrigation water, with a more pronounced impact in regions with two crops rice per year. Flooding treatment enhances soil As activity while decreasing soil Cd activity. Conversely, the growing of unirrigated crops or alternating irrigated/unirrigated crops, or using solely furrow-irrigation methods serves to decrease As activity in rice soils, consequently lowering As uptake by rice plants and its accumulation in the grain. Additionally, water serves as a

carrier for nutrients essential for plant growth, acting as a medium for various biochemical reactions. Water governs the transport and transformation of substances within the soil. The distribution, movement and efficacy of soil water are determined by soil hydraulic performance parameters^[50].

Heat transfer induces alterations in soil temperature, subsequently impacting capacity of plants to absorb water, nutrients and metal(loid) pollutants from the root zone. It also influences the quantity and extent of migration and transformation of these pollutants, as well as the rate of soil water-air transport and its distribution in the soil, consequently influencing the occurrence and transformation of physical, chemical, and biological processes in the soil. The content, state and movement characteristics of soil water, and air heat within metal(loid)-contaminated areas interact with each other. This interaction determines the potential for material exchange between the soil and the environment, as well as its impact on land productivity and related factors^[51]. Metal(loid) pollutants elevate ionic content within contaminated soils. Through oxidation facilitated by irrigation and air exposure, as well as interactions with soil nutrients, they form complexes that alter the structure of soil particle aggregates. Consequently, this restructuring impacts the arrangement of soil pores. In a study, *Aspergillus niger* successfully removed Cr from soil. Remarkably, it achieved 75% removal within 15 days, particularly when the soil water content was at field holding capacity.

2.6.3 Water and fertilizer management and phytoremediation

Research has established that the uptake capacity of plants for metal(loid) contaminant ions in soil is influenced not only by their genetic mechanisms but also by the composition of the rhizosphere microbiota^[52]. Plant roots often absorb a significantly higher amount of pollutants than in the immediate root zone. Typically, water stress induces an elevation in plant root density, resulting in increased exposure of the root system to metal(loid) pollutants. In other words, moderate water stress during non-critical water demand periods leads to an augmentation in root density among hyper-enriched plants, thereby facilitating the uptake and accumulation of metal(loid) pollutants by plant roots. Despite the exceptional drought resistance of certain super-enriched plants, severe water deficits can still reduce their capacity to remediate metal(loid)-contaminated soils.

Hence, understanding the water and nutrient demand patterns of super-enriched plants at each growth stage is of paramount importance in enhancing super-enriched plant biomass and

optimizing water and fertilizer use efficiency, aligning with their growth characteristics. Implementation of water and fertilizer management strategies can augment root system capacity to convey water and nutrients to the canopy, elevate the efficiency of water and fertilizer transfer, stimulate the progression of photosynthesis, and facilitate the conversion of photosynthates to biomass, ultimately aiming to boost the biomass of super-enriched plants. Simultaneously, it is imperative to select the optimal harvesting stage in accordance with the metal(loid) pollution ion uptake patterns during each growth stage of super-enriched plants, as this has substantial scientific merit for the phytoremediation of metal(loid)-polluted soil. Also, there is a need to intensify research efforts aimed at elucidating the mechanisms underlying the regulatory effects of water and fertilizer in the collaborative remediation of metal(loid)-contaminated soil.

2.6.4 Multiple effects of water and fertilizer management

Presently, regions with metal(loid)-contaminated soil have challenges encompassing a fragile ecological equilibrium, decreased soil fertility, and water scarcity. Consequently, the use of water and fertilizer resources becomes markedly inefficient. Also, the ineffective application of nitrogen fertilizers, coupled with their prolonged excessive use, results in substantial environmental stress. The surplus nitrogen in agriculture is a direct cause of surface water eutrophication^[53]. Hence, the pivotal challenge lies in realizing the efficient use of plant water and fertilizer resources to enhance plant biomass and yield. This challenge stands at the forefront of managing agricultural surface source pollution and executing phytoremediation of contaminated soil. Addressing this challenge requires urgently enhancing the biomass and water-fertilizer use efficiency of highly enriched plants. This enhancement is achieved through the implementation of water-fertilizer regulation and water-fertilizer control mechanisms, guided by appropriate fertilizer application aligned with soil moisture conditions. Therefore, important to facilitate, as a matter of some urgency, the remediation of metal(loid)-contaminated soil by highly enriched plants. Using well considered irrigation and fertilizer practices has the potential to substantially augment plant biomass, yield, and water use efficiency.

Conversely, this approach can enhance the tolerance of non-highly enriched plants to metal(loid)-polluted soil environments and mitigate the adverse impacts of metal(loid) pollutants on plant growth. Confronted with the challenge of limited biomass and slow growth in highly enriched plants during the remediation of metal(loid)-contaminated soil, we look to soil water and fertilizer regulation as a breakthrough

strategy. This involves cultivating a more favorable microenvironment (water, fertilizer, air, and heat) within the root zone to expedite the growth of highly enriched plants. This is achieved through suitable water and fertilizer management practices grounded in established engineering, physical, chemical, and agronomic measures. Simultaneously, this could provide a sturdy foundation for enhancing the water and fertilizer use efficiency of highly enriched plants. Progress in this regard serves as a clear basis for maximizing the aboveground biomass of highly enriched plants through well reasoned water and fertilizer management. However, the excessive application of irrigation and fertilizers proves counterproductive, leading to resource wastage and detrimental effects on plant growth. Also, it may result in the migration and diffusion of metal(loid) pollutants into lower soil layers, potentially causing further contamination issues^[54].

Some studies investigate the physical, chemical, and biological changes in soil following pollution, triggered by the application of water and fertilizer control technology. We aim to integrate agronomic, biological, and managerial water conservation techniques to optimize the allocation of water and fertilizer resources for phytoremediation of metal(loid)-contaminated soil. Our goal is to establish a novel phytoremediation model grounded in water-saving irrigation technology and precise water and fertilizer control. Additionally, we will explore diverse approaches to plant growth and fertilizer use based on the most effective soil remediation outcomes. The above discussion seeks to provide innovative strategies for efficient water and fertilizer management across various plant growth stages, emphasizing the optimal remediation of polluted soil^[55]. An imperative objective is to intensify research and development efforts focused on using energy crops for the remediation of metal(loid)-contaminated soil. Future research focus on investigating the interplay between water and fertilizer control technology and its interactive effects on polluted soil, plants, and microorganisms. Henceforth study aims to systematically examine the application model of plant-based remediation, leveraging agronomic, biological, and managerial water conservation techniques in conjunction with precise water and fertilizer control methodologies (Fig. 4).

2.7 Joint remediation techniques

Presently, within the field of soil remediation, single remediation methods like phytoremediation and chemical approaches have certain limitations. Conversely, researchers are increasingly uncovering and elucidating joint remediation techniques (Table 2).

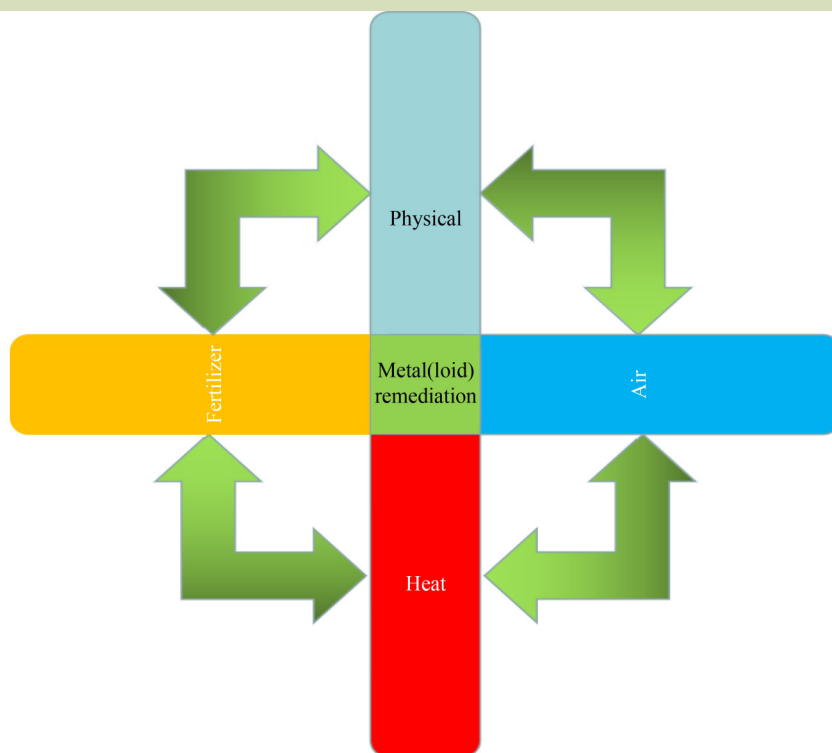


Fig. 4 Typical agricultural management measures.

Table 2 Joint remediation techniques

Joint remediation technique	Remediation mechanism	Advantage
Biochar and phytoremediation	Biochar has the potential to combine with phytoremediation technology due to its strong adsorption and wealthy functional groups, which can promote the growth, enhance the fixation of metal(loid) and promote their uptake	Greener and more efficient
Microbial and phytoremediation	Improve the efficiency of microbial remediation of soil metal(loid) pollution, promote plant extracellular ligand reactions of metal(loid) ions, promote soil metal(loid) enrichment, promote release metabolites by plant	Good remediation and maintenance of the ecological environment
Microbial, phytoremediation, and nanomaterials	Promote plant absorption efficiency and tolerance through a combination of chemical and biological processes, resulting in efficient treatment	Economically efficient
Microorganisms and biochar	Use biochar to make the soil loose and provide more living space for microorganisms, reduce the toxic effects of metal(loid), reduce metal(loid) uptake by seedlings, and increase the structural richness and species diversity of inter-root soil bacterial and fungal communities	Green and highly efficient
Water, fertilization, and other measures	By adjusting soil water, fertilizer, gas (steam), heat, pH, and reduction potential of plant roots, the effective use of water and fertilizer resources by roots can be promoted, and the absorption of metal(loid) pollutants by roots and the transfer	Economically efficient and convenient
Nanomaterials and electrokinetic	Nanomaterials can adsorb soil metal(loid) ions and enhance the transport potential of nanomaterials through electrophoresis,	Environmentally-friendly
Nanomaterials and phytoremediation	Nanomaterials can improve the ability of plants to absorb metal(loid) by reducing their toxicity to plants	Green and highly efficient

2.7.1 Biochar and phytoremediation techniques

Biochar has the potential for integration with phytoremediation technology owing to its robust adsorption capabilities and rich functional groups. Hence, it becomes

imperative to examine the impact of combined remediation on the distribution of metal(loid) in soil with the goal of identifying a more environmentally-friendly and efficient remediation approaches. Some researchers conducted a pot

experiment on biochar and phytoremediation^[56]. They assessed the morphological attributes of plants and the horizontal and vertical distribution of metal(loid) throughout the plant growth phase. The findings revealed that the incorporation of biochar positively influenced the growth of plants. Also, the introduction of biochar facilitated the sequestration of Pb and the uptake of Cd during the growth of plants. This research elucidated the impact of biochar-phytoremediation on the distribution of metal(loid), specifically Pb and Cd, within the soil^[57].

2.7.2 Plant-mycorrhizal fungal microbial remediation techniques

Research has demonstrated that combined plant-mycorrhizal fungal microbial remediation techniques harness the ability of plants to engage in extracellular ligand interactions with metal(loid) ions via soil metal(loid) enrichment. Simultaneously, plants release metabolites through their metabolism, reinforcing their cooperation with metal(loid). This synergistic approach serves to enhance the bioavailability of soil metal(loid)^[58]. Researchers conducted experiments combining arbuscular mycorrhizal fungi with host plants for remediation. The results revealed that this combined approach significantly improved the ability of plants to withstand Cd and Zn stress and absorb these elements. Also, the joint action of mycorrhizal fungi and plants induced alterations in metal(loid) uptake efficiency by plants, thereby indirectly lowering the soil metal(loid) content^[59].

2.7.3 Microbial-plant-nanomaterial remediation techniques

The combined microbial-plant-nanomaterial remediation approach integrates microorganisms, plants, and nanomaterials in agricultural fields, capitalizing on their adsorption capabilities and the synergistic function of microorganisms and plants to facilitate the accumulation of metal(loid) in plants, ultimately remediating the soil^[60]. Researchers conducted a study on remediating soil Cd pollution through the synergistic application of microbial-plant-nanomaterials, demonstrating a substantial reduction in soil Cd content through this combined remediation approach^[61]. Presently, the combined microbial-plant-nanomaterial remediation technique is receiving increased attention^[62]. However, the current body of research remains limited and further research is needed, particularly on ensuring safe application of microorganisms and plant viability, as well as optimizing nanomaterial utilization^[63].

2.7.4 Combining different microorganisms with biochar techniques

Although microorganisms can be used to address soil

metal(loid) pollution individually, their independent remediation efficacy is limited. Therefore, to enhance the remediation of metal(loid) pollution in agricultural soils, microorganisms can be effectively combined with other remediation techniques. This approach primarily involves the comprehensive blending of microorganisms with biochar within metal(loid)-contaminated soil. It capitalizes on the unique properties of biochar, which enhance soil aeration and create a conducive environment for microorganisms. Subsequently, the farmland soil is remediated as microorganisms adsorb metal(loid) from the soil.

Researchers have observed that by combining various microorganisms with biochar for remediation, the synergistic effect of biochar and microorganisms can significantly reduce the bioavailability of soil metal(loid), effectively remediating metal(loid)-contaminated soil. Researchers examined the impact of combining microorganisms and biochar for remediation on the passivation of soil metal(loid). Their findings indicate that this combined remediation approach can substantially decrease soil metal(loid) content and improve their passivation. Additionally, the joint remediation of metal(loid) in agricultural settings using fungi and biochar effectively reduces the uptake of these contaminants by plants. Although the combined application of microorganisms and biochar proves effective in remediating metal(loid)-contaminated soil, it is essential to acknowledge potential safety concerns. Some biochar may contain metal(loid), and the methods for metal(loid) recovery from such biochar are currently a subject of ongoing research.

The application of composite bacteria and biochar of varying particle sizes, either individually or in combination, can lead to varying degrees of metal(loid) fixation in the soil. This approach effectively mitigates the toxic impact of metal(loid), reduces their uptake by seedlings, and enhances the structural diversity and species richness of bacterial and fungal communities in the inter-root soil. Notably, the combination of composite bacteria and micron-sized biochar (particle size range of 1.6–55.8 μm) emerges as the most effective approach in this regard. The combined remediation using hybrid bacteria and micron-sized biochar concurrently promotes plant growth and enhances their antioxidant capabilities^[64]. Also, it leads to a reduction in the proportion of metal(loid) within leaf organelles, resulting in decreased toxicity. Additionally, this remediation approach significantly augments the number of operational taxonomic units for both bacteria and fungi in the rhizosphere soil, leading to increased richness and diversity within the dominant bacterial communities and an overall enhancement of the microbial community structure in the rhizosphere soil.

2.7.5 Microbial and phytoremediation techniques

Among the numerous methods available for addressing metal(loid) pollution, phytoremediation of contaminated soil is particularly effective in remediating soil and preserving the ecological environment^[65]. Nevertheless, the primary drawback of relying solely on plants for soil metal(loid) remediation is their slow growth. This slow growth, coupled with extended remediation periods and limited biomass, results in a relatively modest impact on metal(loid) remediation. Consequently, using a combination of plants and microorganisms for co-remediation purposes can enhance the efficiency of microbial remediation of soil metal(loid) pollution. Researchers have conducted experiments pairing of south-east sedum plants with organochlorine pesticide-degrading bacteria in agricultural soil contaminated with both soil Cd and organochlorine pesticides. The results demonstrated that the combined microbial-plant approach effectively reduced the levels of soil metal(loid) Cd and pesticide. Researchers addressed metal(loid)-contaminated soil through a combination of plants and microorganisms, leading to a reduction in soil contaminants and the eventual remediation of agricultural soils. Based on pot experiments, researchers concluded that combined remediation of plants and microorganisms, along with diverse soil amendment techniques, could effectively decrease metal(loid) concentrations in contaminated soils. Researchers have suggested that a synergistic approach involving plants and Cu-tolerant microorganisms has the potential to remediate Cu-contaminated soils^[66].

2.7.6 Combination of water and fertilization measures with other measures

Microbial remediation involves using active microorganisms to adsorb or transform metal(loid) pollutants into less toxic forms, thereby decreasing the level of soil metal(loid) contamination. Investigating the potential of microbial remediation is a crucial aspect of addressing metal(loid) contamination in soils. Typically, the introduction of water and fertilizers can alter soil structure, adjust soil pH and conductivity, consequently establishing more favorable conditions for the activity and reproduction of microorganisms within the root zone. Consequently, investigating the inter-root microecological environments in areas with contaminated soil under varying water and fertilizer regulation techniques has great scientific significance for the phytoremediation of metal(loid)-contaminated soils. Microbial remediation stands as an indispensable component of the bioremediation approach to addressing metal(loid) contamination in soils^[67].

The integration of water and fertilization techniques with physical, chemical, and biological measures constitutes an effective approach for the phytoremediation of metal(loid)-contaminated soils. In the past, extensive research has focused on individual remediation technologies. However, there has been comparatively less examination of integrated remediation approaches that combine a variety of techniques. Particularly, the use of combined remediation technologies involving high-yield plants, various processes (e.g., plant growth and developmental stages, and the soil-plant-atmosphere continuum system), and multiple techniques (e.g., engineering, physical, chemical, and biological methods) with water and fertilizer as key regulating factors remains unreported. The absorption of pollutants from the soil by plants is influenced not only by the concentration of contaminants in the soil but also by soil characteristics, water conditions, fertilizer types and quantities, plant varieties, cultivation methods, and agronomic practices such as tillage systems^[68]. Hence, by modifying soil parameters, such as pH, cation exchange capacity, organic matter content, and calcium carbonate presence and texture, through water and fertilizer management, the remediation of metal(loid) can be enhanced. This involves the adjustment of soil moisture, fertilizer availability, gas exchange, temperature, pH and the redox potential in the root zone to facilitate the efficient use of water and fertilizer resources by plant roots. This leads to improved absorption of metal(loid) pollutants by roots and their subsequent translocation and accumulation in aboveground plant parts. In addition, by modifying the behavior of metal(loid) pollutants in the soil and reducing their bioavailability through increased adsorption, the transfer of metal(loid) pollutants from the soil to plants can be moderated.

2.7.7 Combined organic acid drenching-electrochemical/photochemical oxidation technique

Research has demonstrated the efficacy of environmentally-friendly small-molecule organic acids, such as citric and oxalic acids, in leaching metal(loid) from soil into the leachate through mechanisms involving solubilization, redox reactions, and complexation. The use of these organic acids as soil extractants for metal(loid)-contaminated sites has promising potential. Building upon these findings, researchers have devised a comprehensive technique that combines the use of small-molecule organic acids for drenching with electrochemical and photochemical oxidation for the remediation of metal(loid)-contaminated soil sites^[69].

Initially, a flow electrode electrochemical system was established, and its feasibility and underlying mechanisms were examined with the aim of treating metal(loid)-laden soil

drenches that included organic acid complexes. The results revealed that the mobile electrode electrochemical system effectively eliminated the metal(loid) complexed with organic compounds from the simulated soil drenches. Also, this investigation confirmed the viability of the electrochemical adsorption and oxidation system in removing organic complexed metal(loid) from soil drenches. It also established a system that combines small-molecule organic acid drenching with manganese oxide electrochemical oxidation for remediating soil at real high-concentration As contaminated sites^[70]. Throughout the drenching and electrochemical removal procedure, there was a substantial reduction in both amorphous and crystalline Fe–Al oxide-bound As levels in the soil. However, the As content in other forms remained relatively stable. Citrate leaching accomplished the removal of As from the soil through solubilization, ligand exchange, and the indirect reduction of As(V). In contrast, within the electrochemical system, the elimination of As from the drench solution was predominantly driven by the formation of hydrous ferrite and δ -MnO on the anode, along with the adsorption of rhodochrosite on the cathode^[71].

2.7.8 Nanomaterials and electrokinetic remediation techniques

When addressing metal(loid) contamination in soil, using nanomaterials and electrokinetic remediation techniques alone often proves insufficient for achieving optimal remediation outcomes^[72]. Consequently, researchers have examined diverse combinations of technologies for remediating soil metal(loid) contamination to attain the most effective remediation outcomes. Nanomaterials are not only used alone but are also integrated with other soil remediation techniques to address metal(loid) contamination in soil. Notable combinations include the integration of nanomaterials with electrokinetic remediation technology and nanomaterials with phytoremediation technology, among others. When combining nanomaterials with electrokinetic remediation technology, nanomaterials are capable of adsorbing metal(loid) ions from the soil while concurrently enhancing their transport capabilities via electrophoresis. This amalgamation harnesses the strengths of both technologies to improve the remediation of soil metal(loid) contamination. An investigation revealed that the electrokinetic process can facilitate the diffusive migration of iron nanomaterials within coarse and medium-grained soils. Additionally, researcher used a combination of electrokinetic remediation and permeable reaction walls to augment the diffusive migration of iron nanoparticles in coarse and medium-grained soils^[73].

2.7.9 Combined nanomaterial and phytoremediation technology

In the remediation of metal(loid)-contaminated soil, a technology involving a permeable reactive barrier with nano zero-valent iron as the primary reactive material has been used. Within this integrated remediation technique, nanomaterials enhance the ability of plants to absorb metal(loid) by mitigating their toxicity to plants. The incorporation of nano TiO₂ into the soil has shown promise in promoting the uptake of metal(loid). This has been primarily attributed to the ability of nano TiO₂ particles to infiltrate plant chloroplasts and engage with the photosystem II reaction center, thereby enhancing electron transport and chloroplast photoadaptation capacity. Consequently, this leads to an increased uptake of Cd, offering a viable strategy to augment phytoremediation efforts. Also, it is worth noting that various factors, including the choice of nanomaterials and application timings, can influence the overall effectiveness of the combined nanomaterial and phytoremediation technology^[74].

2.8 Novel remediation techniques

2.8.1 Zinc oxide nanoparticles

Nanomaterials are increasingly being deployed in both environmental management and agricultural production. Nanotechnology has remarkable potential in addressing metal(loid) contamination in soil. As an illustration, zinc oxide nanoparticles can function as fertilizers, enhancing photosynthesis and crop yield while concurrently mitigating the accumulation of metal(loid) in crops^[75]. If metal(loid)s interfere with the seed germination stage, their adverse effects on yield can be significant. The mechanisms by which nanomaterials alleviate soil metal(loid) stress remain relatively understudied, necessitating further investigation. Additional research is required to devise methodologies for assessing the effectiveness of nanomaterials and to ascertain whether they cause any adverse environmental consequences or have other ramifications^[76].

2.8.2 Zero valent iron

Zero valent iron (ZVI) is extensively used by environmental professionals due to its cost-effectiveness and remarkable efficiency in sequestering metal ions. ZVI has the capacity to immobilize metal(loid) and decrease their bioavailability. This immobilization depends on the reduction capabilities of ZVI and its capacity for adsorption and co-precipitation reactions. Nevertheless, standard ZVI commonly has low corrosion rates, primarily attributed to their relatively limited specific surface

area and the inherent passivation layer that impedes solute-to-ZVI mass transfer^[77]. To overcome this challenge, numerous strategies have been proposed to enhance ZVI corrosion rates. These strategies include acid wash pretreatment, synthesis of nano-ZVI, combining ZVI with activated carbon or zeolite, and introduction of sulfur into ZVI.

Recent studies have demonstrated the capacity of sulfur-modified ZVI (S-ZVI) to concurrently remove As, Cd, and Pb from water. However, the use of S-ZVI in the remediation of metal(loid)-contaminated soil warrants further investigation and validation. Metal(loid) species in soil exist in diverse forms, encompassing not only soluble states but also more intricate and challenging-to-manage granular forms. Consequently, the behavior of metal(loid) and S-ZVI in a soil environment may differ from their behavior in an aqueous environment^[78]. Also, soil physicochemical attributes, including soil pH, texture, and humic material content, can have a profound impact on the immobilization process of S-ZVI within the soil matrix. Also, in the context of mitigating the environmental hazards posed by soil metal(loid), there exists a potential risk of metal(loid) reactivation when alterations in the soil environment transpire, such as shifts in redox conditions. Consequently, it is imperative to conduct detailed research into the long-term transformation and stability of metal(loid) immobilized by S-ZVI. This will be needed for understanding their behavior and fate over extended periods.

2.8.3 Mesoporous materials

Several materials, including mesoporous materials, functional membrane materials, plant polyphenolic substances, and nanomaterials, have distinctive surface structures and compositions that enable them to achieve enhanced remediation when applied at lower concentrations. Research has demonstrated that the application of mesoporous materials to soil results in a reduction of Cd, Pb, and Cu content in the acid-extractable form, an expansion of the organic-bound form, and a substantial reduction in the accumulation of metal(loid) within test chard. Iron phosphate nanomaterials, when applied to remediate soil Cu contamination, notably lowered Cu levels in the water-soluble, exchangeable, and carbonate-bound states. Additionally, they facilitated the conversion of Cu into the residual state. Also, iron nanomaterials provided a substantial reduction in Cr content within the soil drench solution. An experimental investigation into the remediation of soil contaminated with metal(loid) using novel organic–inorganic porous hybrid materials revealed their capacity to notably decrease the levels of Pb and

Cd in the soil extract, as measured by the toxicity characteristic leaching procedure. Additionally, these materials were effective in reducing the accumulation of Pb and Cd in test oilseed rape crops^[79].

2.8.4 Modified biochar

As a new carbonaceous material, biochar is widely used to absorb metal(loid) from soil and water. The impact of modified biochar on the remediation of metal(loid) is attributed to the synergistic effects of multiple mechanisms, including alterations in soil pH, modifications to soil organic matter content, shifts in soil redox potential, and changes in soil microbial community composition. Biochar is particularly useful for adsorbing metal(loid)^[80]. The effectiveness of biochar in remediating soil metal(loid) depends on several factors, including the characteristics and application rate of the biochar, soil fertility and properties, as well as the specific metal(loid) involved^[81]. Consequently, it is imperative to choose appropriate biochar products suited to the predominant types of metal(loid) contamination in various soils to achieve more effective soil remediation outcomes.

Biochar can be categorized based on its source, which may include plant residues and animal waste. Biochar is currently extensively used in agriculture, with numerous studies demonstrating its capacity to decrease the mobility and bioavailability of metal(loid). Biochar is abundant in alkaline substances, hydroxides, nutrients, and other constituents, which can bind with and participate in metal(loid) reactions. Also, owing to its inherent porous structure, numerous functional groups and charged sites, biochar can directly adsorb metal(loid). Biochar can serve as an aggregator for organic matter, including humus, enhancing the stability of metal(loid) through improved electron transfer efficiency^[82]. The highly porous structure of biochar contains substantial quantities of extractable humus and xanthate-like compounds. The enhancement of soil aggregates following biochar incorporation is typically ascribed to the increased presence of oxidized functional groups following biochar mineralization. This, in turn, facilitates the flocculation of soil particles and biochar. Also, the pH levels of soils amended with biochar are more supportive of microbial growth, particularly fungal mycelium. A study demonstrated that augmenting the soil with additional biochar creates a more favorable habitat for microorganisms, thereby fostering their growth through enhanced porosity. Research and development of biochar for the improvement of agricultural soils and crop cultivation should be intensified. This endeavor should encompass a deeper examination of the mechanisms governing biological

and chemical reactions in metal(loid)-contaminated soils. Additionally, it should entail conducting field studies and long-term investigations into the effects of biochar application.

2.8.5 Organic framework composites

The environmental applications of biomass nanocellulose-based metal organic framework composites (MOFs@NC) in soil remediation and air purification has significant potential. MOFs@NC not only preserves the high adsorption capabilities of metal organic frameworks (MOFs) and the environmental stability of MOFs@NC but also benefits from the highly entangled MOFs@NC scaffold on the nanoscale, facilitating the complete dispersion of MOFs. This enhances composite flexibility, enabling it to achieve effective adsorption, efficient catalysis, and precise separation of environmental pollutants, including metal(loid), organic compounds, and gas particles. Additionally, the MOFs@NC scaffold allows dispersal of MOFs and improving the elasticity of the composite material, resulting in effective adsorption, efficient catalysis, and precise separation of environmental pollutants like metal(loid), organic compounds, and gas particles. Future research directions encompass the investigation of (1) the synthesis mechanism and physicochemical properties of MOFs@NC, (2) the removal of metal(loid), organic pollutants, and particulate matter, along with their applications in gas separation, and (3) the mechanisms underlying the adsorption, degradation, and separation of pollutants. Three representative mechanisms of pollutant removal, such as adsorption [including metal(loid)s and organic pollutants], are evident. In soil treatment, the its high specific surface area and chemically modifiable surface functional groups enable MOFs@NC to efficiently adsorb metal(loid) ions and organic pollutants. Additionally, the transition metal centers within MOFs composites facilitate the efficient catalysis of organic pollutant degradation^[83].

Despite significant progress in the preparation and application of MOFs@NC, numerous challenges and opportunities persist in the field of environmental remediation. These include the need for green, efficient, and cost-effective methods to prepare MOFs materials, as well as the examination of more economical drying techniques for the production of MOFs@NC composite aerogels. Also, attention should be given to improving the water stability of MOFs and examining in detail the mechanisms of interaction between NC and MOFs. Enhancing the performance of MOFs@NC composites and enabling large-scale production for environmental applications are also areas of focus^[84].

2.8.6 Tobacco waste

Research has revealed that tobacco waste generated during the tobacco production process contains a significant amount of organic matter. This organic matter can be effectively and inexpensively converted into hydrothermal carbon adsorbents, suitable for the removal of divalent Cd and the remediation of Cd-contaminated environments using hydrothermal carbonization methods. Nevertheless, the challenge lies in the separation of hydrothermal carbon from water and soil. Iron slag, a byproduct of steel production, possesses strong magnetic properties. Consequently, it becomes feasible to impart magnetic characteristics to hydrothermal carbon through co-hydrothermal treatment with waste iron slag and tobacco waste liquor, thereby simplifying its separation process. Embracing the concept of treating waste with waste and guided by the principles mentioned above, researchers used tobacco waste and iron slag as raw materials to produce iron-based carbon microspheres for the purpose of remediating Cd pollution in water and soil. It is worth noting that these two waste materials, when repurposed in this manner, should lead to a decreased environmental burden. Research has shown that the surface of iron-based carbon microspheres has carboxyl groups, aromatic rings and other functional groups, along with Ca ions. These components collectively facilitate the removal of Cd through mechanisms such as cation- π bonding, electrostatic attraction and cation exchange^[85].

2.8.7 Exogenous chelating agents

Maintaining high soil environmental quality is essential for safeguarding the quality and safety of agricultural products. An effective approach for remediating Cd-contaminated soil involves using metal(loid)-enriched plants supplemented with exogenous chelating agents. Among the various chelating agents available, low-molecular-weight organic acids stand out due to their minimal adverse impact on plants and the soil microenvironment. Simultaneously, they facilitate the uptake of Cd by plant roots, making them highly promising for soil remediation. The application of exogenous organic acids in Cd-contaminated soil led to increased biomass in the enriched plant, specifically oleander. However, the extent of enhancement varied depending on the type of plant^[86]. The introduction of exogenous organic acids resulted in enhanced Cd extraction by plants. However, it did not lead to increased Cd enrichment in seeds. Interestingly, it did contribute to reducing the Cd content in the soil surrounding the roots. Also, the application of organic acids had the effect of decreasing nutrient and salt levels in the soil surrounding the roots, concurrently promoting the uptake of soil nutrients by the root system of plants^[87].

2.8.8 Exogenous spraying of Fe₃O₄ and ZnO nanoparticles

Cd stress profoundly impacts various aspects of tobacco, including primary metabolism, secondary metabolism, energy metabolism, and ion homeostasis, resulting in a severe inhibition of tobacco seedling growth. The application of Fe₃O₄ and ZnO nanoparticles as foliar sprays enhanced nutrient uptake by plants and effectively reshaped critical primary and secondary metabolic pathways, ultimately fostering plant growth. Subsequent analysis demonstrated that the majority of differential metabolites observed in both roots and leaves under Cd stress returned to normal growth levels following the exogenous application of nanoparticles. This restoration of essential metabolites suggests that nanoparticles effectively mitigated the toxic impact of Cd on tobacco seedlings. Notably, nanoparticles had superior alleviating effects compared to their corresponding metal ions. Also, correlation analysis unveiled that certain metabolites, including alkaloids, flavonoids, amino acids, nicotinic acid, and nicotinamide, had a more pronounced impact on plant response to Cd stress^[88].

2.8.9 Lignin hydrogel

Lignin hydrogel (FeS@LH), when enriched with nano-FeS, has proven to be highly effective in reducing Cd levels in contaminated agricultural soils and vegetables, achieving a reduction of over 30%. Additionally, it enhances soil carbon and nitrogen nutrient levels and facilitates the gradual restoration of soil microbial populations. This study offers both theoretical insights and practical applications for hydrogel composites in addressing metal(loid) pollution in soil^[89]. The incorporation of FeS nanoparticles into lignin hydrogel resulted in impressive Cd adsorption capabilities, coupled with remarkable mechanical strength. A simulation study systematically examined the principal adsorption mechanism of the composite for Cd in Cd-contaminated paddy environments, and ultimately affirmed the effectiveness of the material for metal(loid) decontamination^[90].

2.8.10 Biochar substrate as Mn-N₄

Mn is firmly anchors onto a biochar substrate, forming Mn-N₄ coordination. This monoatomic material has an exceptional capacity for photocatalytic degradation of metal(loid) pollutants, achieving complete degradation of substances while maintaining excellent cycling stability. Experimental investigations, including electron paramagnetic resonance analyses, have unveiled the capability the material to generate a substantial quantity of hydroxyl radicals in the presence of light. This process is oxygen-dependent, and its capacity to degrade metal(loid) pollutants is markedly hindered under oxygen-depleted conditions. Through *in situ* X-Ray

Absorption Fine Structure experiments and molecular dynamics calculations, the research team has unveiled the molecular mechanism underlying the catalytic degradation of pollutants. Under aerobic conditions, oxygen molecules adhere to the Mn monoatomic active center, inducing a change in the Mn valence state from II to IV. In this process, the monoatomic Mn effectively catalyzes the dissociation of oxygen molecules, leading to the release of hydroxyl radicals that accelerate the rapid degradation of metal(loid) pollutants. This study offers a novel perspective on harnessing phytohyperaccumulator biomass as a valuable resource and explores the synthesis and practical application of cost-effective single-atom materials^[91].

2.8.11 Layered double hydroxides

Metal(loid) pollution is one of the most pressing environmental challenges today, characterized by significant ecotoxicity and associated health risks, making it a formidable issue to address. Some metal(loid) ions form strong bonds with N, O and S atoms within biological molecules, capable of impairing biological functions and obstructing physiological processes, even at trace concentration levels. Consequently, the development of effective methods for detecting and adsorbing metal(loid) is of paramount importance. Layered double hydroxides (LDHs) materials have immense promise for the detection and adsorption of metal(loid) owing to their customizable structure, modifiable lamellae composition, and expansive specific surface area^[92]. In recent years, researchers have introduced a range of LDHs-based probes and adsorbents designed for metal(loid) analysis. In pursuit of enhanced LDHs performance for metal(loid) detection and adsorption, researchers have predominantly achieved this by modifying LDHs materials to augment their specific surface areas and increase their affinity for metal(loid)^[93].

3 Integrated evaluation of various remediation technologies

Evaluating the effectiveness of remediating metal(loid)-contaminated soil involves the integration of effective chemical analysis methods. This evaluation also includes observing the impact on various species and biological components within the soil ecosystem. It aims to qualitatively or quantitatively predict the potential harmful effects of pollutants in the remediated soil on both the soil ecosystem and human health.

Throughout the restoration process, there will be alterations in the physical, chemical, and biological characteristics of the soil.

It is important to note that a reduction in target pollutants does not automatically imply that the soil is environmentally pristine or safe. Consequently, there is a crucial need to establish a comprehensive evaluation standard or system. This system is designed to assess the success of remediating contaminated farmland soil, determine if the intended remediation objectives have been met, ascertain whether soil ecological functions have been restored, evaluate the feasibility of reclamation and ensure that the agricultural products grown on the soil have reached safe levels.

Before the establishment of pollution soil remediation standards, it is imperative to conduct research on the evaluation index system for assessing the effectiveness of pollution soil remediation. In several developed nations, the evaluation of polluted soil remediation effectiveness often involves comparing the levels of target pollutants detected in the soil with permissible concentrations derived from land use purposes and risk assessments. However, this approach may not provide a comprehensive assessment of the ecological safety achieved through soil remediation.

Assessing the remediation effect of polluted soil can be approached in two ways: through the observation of the post-remediation effects on the soil; and through risk assessment. Based on the functional restoration indicators of the remediation objectives, the observation of post-remediation effects on contaminated soil can be categorized in two aspects: biochemical toxicology observation; and ecological indicator observation.

Biochemical toxicology observation depends on assessing the potential harm posed by residual soil metal(loid) to the biological, physiological, and biochemical facets of the environment. It involves measurements at molecular or cellular levels to gauge risk magnitude and evaluate remediation effectiveness, offering high measurement sensitivity and shorter analysis cycles. Ecological indicator observation, by comparison, involves the introduction of sensitive organisms (such as plants, soil animals, and microorganisms) into the remediated soil using soil metal(loid) diagnostic techniques. It assesses soil remediation effectiveness by observing changes in their physiological and ecological characteristics. Commonly used indicators for monitoring the post-remediation effects of polluted soil include plant absorption toxicity indicators, biochemical-level toxicity effect indicators, soil animal absorption toxicity indicators, pollutant migration indicators, soil enzyme level indicators, soil microbial indicators, and biomarker methods. However, the analysis and measurement

methods for these indicators have yet to establish unified standards and specifications. Also, practical application in China is constrained by its vast territory and diverse soil types.

Risk assessment involves predicting the potential adverse ecological consequences of environmental pollutants on either entire ecosystems or specific components thereof. Conversely, soil ecological risk assessment specifically concentrates on the potential repercussions of environmental contaminants infiltrating the soil. This assessment includes at least two primary aspects: human health assessment, with a core focus on human well-being; and ecological health assessment, emphasizing the stability of soil ecosystems and their constituents.

The following six points merit particular attention.

- (1) The selection of evaluation indicators should be determined based on the unique characteristics of each restoration project. These indicators should strive to align with the intended land use function post-restoration, all while effectively mitigating the risk of secondary pollution during the restoration process.
- (2) Among the previously proposed indicator systems, it is essential to distinguish between constraint indicators and reference indicators. Constraint indicators represent the specific objectives that must be attained post-remediation, while reference indicators function as supplementary targets for assessing the efficacy of polluted soil remediation.
- (3) During the assessment of restoration effectiveness, it is crucial to adopt a stringent approach. Even if the soil quality aligns with the anticipated objectives post-restoration, it cannot be deemed fully remediated and suitable for reclamation if the agricultural products grown on it fail to meet the predetermined standards.
- (4) Evaluation indicators should be established for assessing soil remediation effectiveness. Some of these indicators come with predefined evaluation standards that facilitate the assessment process.
- (5) It is important to use analytical methods for each indicator that align with national or industry standards as a primary choice. In cases where standard methods are unavailable, ISO or EPA-recommended methods could be adopted. If no suitable methods are found, academically recognized methods can be used for analysis, with the caveat that their applicability should be thoroughly assessed and explained.

(6) It is essential to assess the need for long-term tracking, monitoring, and evaluation of remediation effects, considering the unique characteristics of each remediation project. Also, specific long-term tracking, monitoring, and evaluation plans should be developed accordingly.

Evaluating the effectiveness of remediating metal(loid)-contaminated agricultural soil includes compliance with laws, regulations, standard systems, guidelines, and norms. It also spans across multiple disciplines, including soil science, ecology, and toxicology. The assessment of the remediation effectiveness of metal(loid)-contaminated soil depends on the establishment of soil remediation standards, with these standards rooted in soil remediation benchmarks. Therefore, it is imperative to intensify research on pollutant thresholds in soil, considering aspects like pollution ecotoxicology and human health, to furnish essential data and a scientific foundation for the formulation of soil remediation standards.

4 Reflections and recommendations

4.1 Exploring new approaches for metal(loid) remediation

In the quest for effective metal(loid) remediation, various factors such as environmental conditions, cost considerations and potential risks associated with modifiers demand a fresh perspective. Researchers must search for innovative materials, technologies and methods to unravel the molecular mechanisms underlying metal(loid) toxicity and detoxification in plants. Simultaneously, they should explore strategies for bolstering plant resilience against metal(loid) stress and reducing toxic metal accumulation through genetic improvement.

4.2 Harnessing genetic engineering

Genetic engineering emerges as a promising avenue to enhance the phytoremediation capabilities of hyperaccumulator plants. By manipulating plant genetics, their metal(loid) uptake and tolerance can be optimized.

4.3 Microbial strain selection and safety

Although expanding the selection of resilient microbial strains is essential, it is imperative to emphasize the safety and controllability of these strains in practical applications. Robust screening processes can help identify strains with solid resistance to metal(loid) toxicity.

4.4 Holistic remediation approaches

Agronomic management measures, screening of more resilient microbial strains, and integration of molecular biology techniques and genetic engineering offer holistic approaches. Combining physicochemical and phyto-microbial remediation methods can yield promising results.

4.5 On-site applications and technical systems

For on-site applications, innovative methods like microbial inoculation through soil spraying can be developed^[94]. Establishing comprehensive technical systems encompassing plant nurseries, cultivation practices, field management, agronomic adjustments, safe disposal, harvesting and resource utilization is essential for successful metal(loid) remediation efforts^[95].

4.6 Advancements in phytoremediation equipment and techniques

Efforts should be directed toward the research and development of comprehensive phytoremediation equipment. This includes enhancing mechanization to reduce remediation costs and improve efficiency. Strengthening technical collaborations and leveraging various technological advantages are crucial steps. Further innovation in remediation methods should be encouraged, with a focus on applying efficient and cost-effective approaches designed to local conditions.

4.7 Rapid advancements in pollution assessment techniques

Accelerating the research and development of rapid investigation, monitoring and assessment techniques and equipment for soil pollution is important. Additionally, there is a need to fortify the establishment of information systems dedicated to soil environment management in agricultural lands.

4.8 Understanding combined toxicity and new pollutants

Vigilance is essential when dealing with combined toxicity and the toxicological characteristics of emerging pollutants, particularly when they interact with metal(loid). This includes specific interactions like those between micro-nano-plastics and environmental pollutants. Understanding the inherent

properties of pollutants is crucial in regulating their colloidal behavior. Additionally, changes in the environmental fate of

micro-nano-plastics induced by metal(loid) pollution should not be overlooked.

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Compliance with ethics guidelines

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