



Review article

Past, present and future trends in the remediation of heavy-metal contaminated soil - Remediation techniques applied in real soil-contamination events



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ABSTRACT

Most worldwide policy frameworks, including the United Nations Sustainable Development Goals, highlight soil as a key non-renewable natural resource which should be rigorously preserved to achieve long-term global sustainability. Although some soil is naturally enriched with heavy metals (HMs), a series of anthropogenic activities are known to contribute to their redistribution, which may entail potentially harmful environmental and/or human health effects if certain concentrations are exceeded. If this occurs, the implementation of rehabilitation strategies is highly recommended. Although there are many publications dealing with the elimination of HMs using different methodologies, most of those works have been done in laboratories and there are not many comprehensive reviews about the results obtained under field conditions. Throughout this review, we examine the different methodologies that have been used in real scenarios and, based on representative case studies, we present the evolution and outcomes of the remediation strategies applied in real soil-contamination events where legacies of past metal mining activities or mine spills have posed a serious threat for soil conservation. So far, the best efficiencies at field-scale have been reported when using combined strategies such as physical containment and assisted-phytoremediation. We have also introduced the emerging problem of the heavy metal contamination of agricultural soils and the different strategies implemented to tackle this problem. Although remediation techniques used in real scenarios have not changed much in the last decades, there are also encouraging facts for the advances in this field. Thus, a growing number of mining companies publicise in their webpages their soil remediation strategies and efforts; moreover, the number of scientific publications about innovative highly-efficient and environmental-friendly methods is also increasing. In any case, better cooperation between scientists and other soil-related stakeholders is still required to improve remediation performance.

1. Introduction

Soil is a non-renewable natural resource which can be considered as the most essential component of terrestrial ecosystems. Unfortunately, soil is also a major sink for pollutants of different nature like heavy metals (HMs), which are persistent contaminants since

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they can neither be degraded nor destroyed. These elements occur naturally in the Earth's crust in various forms of the solid phase of soils and sediments and also dissolved in water. Low concentrations of several HMs, i.e. iron (Fe), copper (Cu), cobalt (Co), zinc (Zn), nickel (Ni), manganese (Mn), selenium (Se) and molybdenum (Mo) are necessary for metabolic activity, whilst high concentrations are toxic for humans, plants and microorganisms. Other HMs, such as silver (Ag), arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg) and chromium ($\text{Cr}_{(\text{VI})}$) do not have a known biological function and may provoke serious toxic and carcinogenic effects, even at low concentrations, and thus, they are amongst the priority metals for public health concern [1]. The most common hazards for humans related to soil contaminated with HMs include direct inhalation of particulate matter, dust or aerosols, and ingestion of contaminated water or vegetables [2,3,4]. The toxicity of HMs in soil does not only depend on their total concentration, but also on the bioavailable fraction. This bioavailability depends on numerous factors such as soil pH, organic matter content, temperature, etc. [5]. With all these considerations, it is not surprising that threshold values for HM concentrations in soil are difficult to evaluate [6]. As an example, in the mainland of China, the limit for Pb in agricultural soil is $\leq 250 \text{ mg kg}^{-1}$ ($\text{pH} < 6.5$), $\leq 300 \text{ mg kg}^{-1}$ ($\text{pH} 6.5\text{--}7.5$) and $\leq 350 \text{ mg kg}^{-1}$ ($\text{pH} > 7.5$). In many cases, the authorities establish different thresholds for HM depending on the soil use, with more restrictive levels in the case of agricultural soil [7]. Regulatory concentrations of toxic metals in agricultural soil differ amongst countries; e.g., the limit for Pb is $\leq 300 \text{ mg kg}^{-1}$ in Australia, $\leq 70 \text{ mg kg}^{-1}$ in Canada, or $\leq 200 \text{ mg kg}^{-1}$ in the European Union.

Some soils are naturally enriched in HMs; however, certain anthropogenic activities contribute to the redistribution of HMs, generating relevant environmental and/or human health risks when exceeding certain concentration levels [8,9,10,11,12,1]. Mining activities and mineral processing are sources of large volumes of metal-rich waste materials which generate large extensions of mine tailings and huge volume sludge dams (Fig. 1). Atmospheric deposition of dust emitted during mining exploitation, industrial production, and motor vehicle usage, as well as abandoned contaminated bare soils are other important sources of contaminants [13,14]. Although, lately, mining industry tends to enhance its production rates by using safer and more efficient production methods for reconciling the increase in metal demand (as a result of both a growing world population and potential higher per-capita requirements) with safety [15,16], contamination episodes are inevitable. Another significant anthropogenic source of HMs in agricultural soil is related with certain agronomic practices such as the long-term application of pesticides, fertilizers or irrigation with wastewaters, among others (Fig. 1). Plants acquire metals from soil for their normal development, however, because of the lack of specificity of the uptake mechanisms, when growing in contaminated substrates, they may incorporate toxic concentrations of essential and non-essential HMs [17]. Contamination can also reach plant aerial tissues when the HMs are deposited directly on above ground biomass. As plants are the first compartment of the terrestrial food chain, HM content in plants should be monitored and minimized as soon as possible [18,7].

There are more than 10 million sites with polluted soil reported worldwide, with more than 50% of them contaminated with HMs and/or metalloids. In Europe, there are 2.8 million sites potentially contaminated with HMs; in China, 19% of the agricultural soil contains harmful pollutants and in India, 80% of the contaminated soil has anthropogenic origins in the states of Maharashtra, Gujarat, and Telangana [19,20,21]. The economic impact of HM pollution worldwide has been estimated at more than US \$10 billion per year [13]. The cost and duration of soil remediation are technique-dependent and site-specific, but it has been estimated to be up to \$500 ton^{-1} soil and 15 years [6]. Given the global increase in human population, and thus, the need to maintain soil potential and a high quality food and fiber production in the long term [22], the application of occasional or continuous remedial actions are clearly

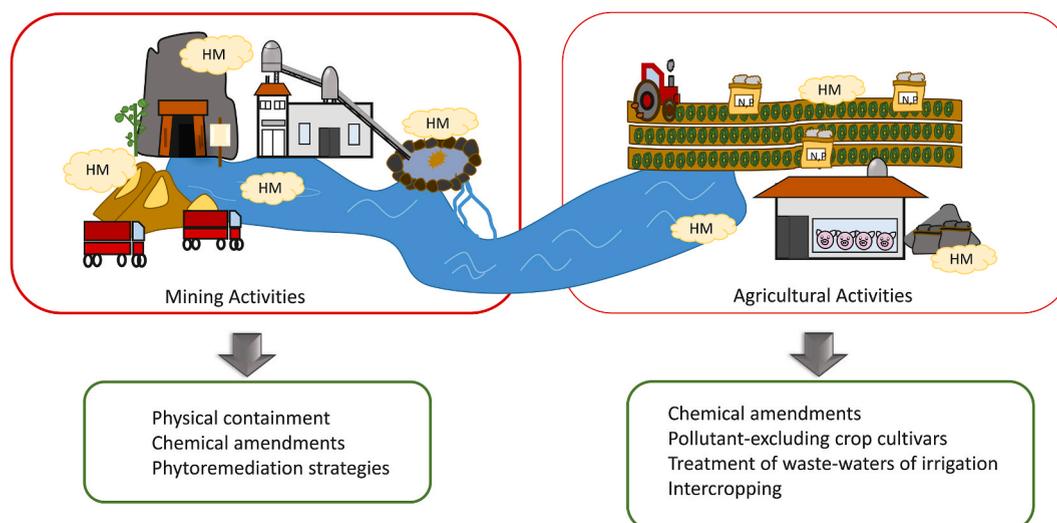


Fig. 1. Schematic representation of the main sources of anthropogenic HM contamination; mining activities generate residues that are in many occasions accumulated in ponds. During these mining activities, in abandoned mines or because of accidents, these HM can be spread by water or air, affecting the nearby areas. Agricultural processes, such as mechanical management, and use of chemical fertilizers, animal manure, or contaminated wastewaters, are also sources of contamination. The main remedial actions that have been demonstrated their utility at large scale are indicated in the lower part of the figure.

Table 1
Frequently used heavy metal remediation techniques.

	Technique	Main characteristics	Advantages	Disadvantages
Physical methods (mainly used to remove the pollutants from soil or to stabilize them for preventing its uncontrolled spread in nature)	Excavation and land filling (<i>ex-situ</i>)	Transport of the contaminated soil to a secure landfill for long term disposal and/or further treatment	- Complete amelioration of HMs	- Time-consuming - High economic cost - Non-aesthetically pleasing - Removed contaminated soil need further handling and disposal
	Surface capping (<i>in-situ</i>)	Coverage of the contaminated soil with a waterproof material forming a stable protection surface	- Fast and easily applicable - Low economic cost	- Generation of solid wastes - Non-aesthetically pleasing
	Encapsulation (<i>in-situ</i>)	Containment of polluted soil with a physical barrier	- Fast and easily applicable - Low economic cost - High safety	- Non-aesthetically pleasing
	Thermal desorption (<i>ex-situ</i>)	Treatment of the contaminated soil at a high-temperature (1400–2000 °C) for separation of certain volatile compounds, such as Hg and As.	- Fast treatment process - High efficiency - High safety - Lack of secondary pollution - Recycling of soil and HMs	- High economic cost - Requires excavation - The heating temperature and the oxygen content of the atmosphere may lead to side reactions
	Vitrification (<i>in-situ</i>)	Heating the polluted soil with high power currents up to the melting temperature. The progressive heating destroys organic contaminants and removes volatile and semi-volatile metal compounds. After cooling the melt forms a glassy product that immobilizes the inorganic contaminants.	- High efficiency	- High economic cost - Loss of soil environmental functions
	Electrokinetics (<i>in-situ</i>)	Removal of ionized metals from wet contaminated sediments by electrical adsorption	- High control of the process - Applicable to all metals - Possibility of treating soils of low permeability, inaccessible to other remediation techniques - Low soil disturbance	- Time-consuming - Low efficiency - Potential acidification of the soil
Chemical methods (Using chemical reactions (e. g. precipitation, redox transformation, ion exchange), to modify the mobility and bioavailability of contaminants)	Chemical solubilization (<i>in-situ</i>)	Application of amendments (mainly organic acids) aimed to increase HM solubility and bioavailability	- Suitable for severely contaminated soil	- May cause secondary pollution
	Chemical stabilization (<i>in-situ</i>)	Application of amendments (e.g. activated carbon, silica, limestone, fly ash) to alter the soil chemistry for precipitating and/or sequestering HMs, minimizing their incorporation to plants as well as leaching into groundwater	- Easy to implement - Quick results - Low economic cost	- Temporary effectiveness
	Redox transformation (<i>in-situ</i>)	Mobilization/immobilization of metallic compounds thorough redox reactions	- Wide range of applications - Suitable for severely contaminated soil	- High invasivity to the soil and the environment

(continued on next page)

Table 1 (continued)

	Technique	Main characteristics	Advantages	Disadvantages
		induced by addition of certain substrates		<ul style="list-style-type: none"> - High economic cost due to the need for large quantities of chemicals - Limited efficiency in low permeability soils
Mixed physico-chemical methods	Soil washing (<i>ex-situ</i>)	Contaminant solubilization as metal ions and transfer from soil to washing fluid for treatment (precipitation or flocculation of HMs)	<ul style="list-style-type: none"> - Low economic cost - Simple implementation - High efficiency - Suitable for severely contaminated soil 	<ul style="list-style-type: none"> - Contaminants are not destroyed and an additional treatment is required - Potential groundwater pollution
Biological methods (To remove or stabilize the contaminant; they are environmentally friendly, aesthetic and economically viable. However, many of them cannot be applied in highly contaminated soils, as they depend on living organisms).	Micro-organisms-mediated (<i>ex-situ, in-situ</i>)	<p>Biosorption: Metabolism-independent reactions. Sorption of HM ions onto the binding sites of microbial cell walls. It does not require nutrients and toxicity by HM does not affect the microbial performance</p> <p>Biotransformation: Transformation of metals, mainly through redox conversions of inorganic forms coupled to microbial processes such as metal-compound respiration or through a dissimilatory sulphate reduction.</p> <p>Volatilization: conversion of metals to volatile derivatives (methyl- and hydride derivatives)</p>	<ul style="list-style-type: none"> - Applicable to most metals - Low economic cost - Non-invasive to the environment 	<ul style="list-style-type: none"> - Low efficiency - Not applicable for highly contaminated soil - Dependent on weather and climatic conditions
	Plant-mediated (<i>in-situ</i>)	<p>Phytoextraction (or phytoaccumulation): metal-accumulating plants translocate and concentrate HMs into their different vegetal tissues. When HMs in aerial parts of plants exceed critical levels, this biomass must be harvested and treated adequately through a variety of methods such as composting or pyrolysis</p> <p>Phytostabilization: reduction of the HM bioavailability in soil by the action of certain plant species. The metal pollutants are first absorbed/precipitated and then accumulated into/onto the roots or in the rhizosphere.</p> <p>Phytovolatilization: Plant species uptake water-soluble HMs from the soil and release them by evaporation or volatilization into the air surrounding the plant</p> <p>Rhizofiltration: Absorption of HMs onto/into plant roots</p>	<ul style="list-style-type: none"> - Applicable to most metals - Low economic cost - Simple implementation - Aesthetically pleasing 	<ul style="list-style-type: none"> - Not applicable for highly contaminated soil - Limited to top layer - Low efficiency - Food chain could be adversely affected - Time-consuming

Ex-situ technologies require the excavation of contaminated soil, transport to the treatment area and disposal of the treated soil at permitted locations. In general, the process can be more controlled and can achieve better results in a shorter time than other techniques; however, they are expensive and soil disruptive. **In-situ technologies** are carried out at the contaminated site, soil disturbance is minimized, and there is less exposure of workers and citizens to the contaminants than in the *ex-situ* technologies; furthermore, the treatment is considered cost-effective. Numerous reviews are available for further information [54,19,40,55,37,56,57,58,59,38,60,61,39].

recommended. In general, the treatments applied to HM contaminated soil aim to reduce the metal fractions of the soil (total and/or available) and to diminish its transfer rate to edible plant parts, as well as to improve soil structural stability to reduce erosion [23,24,25]. Amongst the remediation techniques available, those based on biological methods are generating great interest as demonstrated by the high number of scientific publications in the area [26]. However, bioremediation practices in real scenarios have not generally been well documented from the scientific point of view. Fortunately, industries, politicians and citizens are increasingly aware of the environmental risks and implementation of safety practices are commonly reported on the web pages of many industrial companies. This review covers information on remediation strategies of HM-contaminated soil in real scenarios, based on representative case studies that, at least to some degree, have been scientifically reported. We have also reviewed few cases of remediation on agricultural fields, although, as HM contamination of agricultural areas is an emerging problem, not many open-field experiences have been reported in scientific literature so far. Finally, we present several perspectives for this field in a sustainable development context.

2. Remediation of areas affected by mining activities

Huge volumes of HM-rich waste are generated during mining activities (several thousand million tons per annum) and many are stored in vast areas as tailing dams whose management is considered challenging [27]. Repeatedly, structural problems in dams, produced by construction deficiencies or overload issues, have caused the collapse and the subsequent spread of HM-rich materials into large areas [28,29]. The continuous exposure of minerals or waste material to air and water may cause deleterious effects in mine soils and in the surrounding areas (Fig. 1). The mining of certain minerals (such as gold [Au], Cu, Ni) is commonly associated with subsequent acid drainage problems generated by the geochemical weathering of acid-labile minerals and the chemical oxidation of pyrite and other sulphidic minerals when exposed to air and water [30,31]. These processes can be accelerated by the action of microorganisms such as *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans* [32] and by some of the chemicals used in mining operations (for example, sulphuric acid). Although every mine is unique in terms of its acid mine drainage (AMD), AMD is characterized by low pH and high levels of metals and sulphates.

Once mines are not profitable anymore, the extraction activities cease and the mining facilities are dismantled. Historically, the application of rehabilitation programmes in these areas has not been mandatory by law, and consequently, there are huge inventories of abandoned mines (more than 200,000 in the USA [33], or 6,000 in South Africa [34]) to be restored. In these cases, land recovery is mainly a governmental issue, as many companies have disappeared or have declared bankruptcy, and budget constraints may limit the number of actions that should be undertaken. Mining areas which contain large deposits of mine waste, as well as polluted bare soil without plant coverage, or with conditions for plant development seriously compromised, are exposed to erosion and leaching episodes and pose serious environmental concern [35,36].

The main objective of mine soil reclamation is preventing human and wildlife exposure to contaminants and the stabilization of

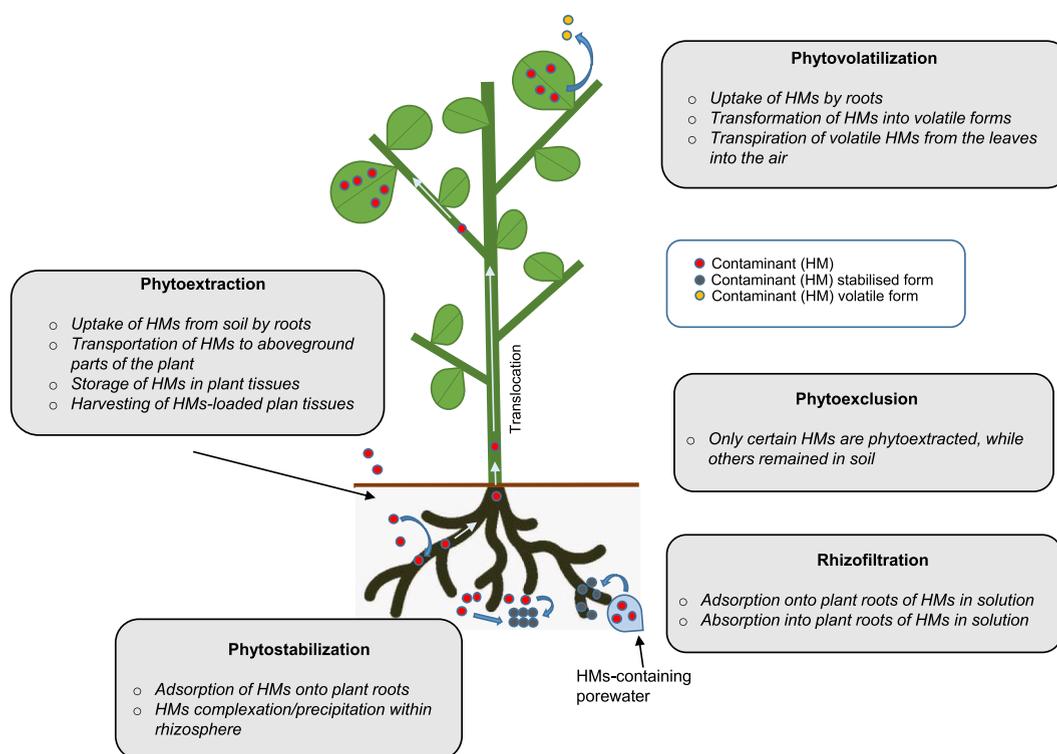


Fig. 2. Schematic representation of the main phytoremediation strategies.

Table 2
Different processes performed during phytomining.

	Methods	Advantages	Disadvantages
1. Phytoextraction	See Table 1		
2. Concentration	Composting (<i>54–60° C with oxygen</i>)	- Ecofriendly - Reduction of the water content - Low cost	- Time-consuming (2–3 months) - Undesirable leachates
	Pyrolysis (<i>300–700° C without oxygen</i>)	- Fast process	- High energy input - Specialized machinery needed
	Gasification (<i>700–1000° C with oxygen</i>)	- Fast process	- High energy input - Undesired products (tars, CO, NO _x , others) - Environmental problems (use of syngas rich in HMs)
	Combustion (<i>> 900° C with oxygen</i>)	- Fast process	- High energy input - Undesired products (CO, NO _x , fly ash, gaseous metal compounds)
3. Extraction	Ashing (<i>300–500° C</i>)	- Fast process	- High economic cost and technical requirements - High energy input
	Pyrometallurgy (<i>Thermal method as incineration, vacuum carbon-thermal reduction, and chlorination volatilization</i>)		- Poor recovery rate - Release of noxious volatile gases - High initial investment required
	Hydrometallurgy (<i>Metals leaching by using acids with later separation and purification by solvent extraction, ion adsorption, ion exchange, and precipitation</i>)	- Higher metal recovery rates - Better selectivity of metals - Low cost - Less contaminant	
	Biometallurgy: bioleaching (<i>using microorganisms</i>)	- Ecofriendly (low toxic emissions) - Low cost	- Poor leaching rate and long operation time (tested at laboratory scale)
	Biometallurgy: biosorption (<i>using biomaterials</i>)	- Ecofriendly (low toxic emissions) - Low cost (most affordable-cost choice for the extraction of ionic forms of metals from liquid phases)	
	Other emerging methods: - Mechano- and electro-chemical technologies - Extraction with ionic liquids - Supercritical fluid techniques		

Different concentration and extraction methods applied during phytomining are described in this table as well as their main advantages and disadvantages.

mine waste products, so they no longer move or become exposed to water and air. Main physical processes commonly used in the management of these soils include land filling, surface capping and encapsulation (Table 1). These techniques require intense mechanical actions on site which may alter the physical soil structure, and also affect its natural biological activity [19,37,6,38,39], and are considered very disruptive to the treated site as well as relatively expensive. Nonetheless, in mining areas where the soil has already been disrupted, these methodologies may clearly contribute to the stabilization of the contaminants. Thermal desorption, vitrification and electrokinetics are other physical methods that have been proposed for the restoration of those soils (Table 1). However, to our knowledge, they have not been employed in mine soil reclamation, probably because their high economic cost and logistic difficulties for treating large surface areas. Chemical methods are mainly used for solubilization, stabilization or redox transformation of HMs (Table 1). Inorganic materials, such as lime, phosphate-based compounds, or fly ash, and also organic amendments such as biochar, biosolids, compost, or manure, are applied to buffer the soil pH, reduce HM availability and improve nutritional status, water-holding capacity, and soil structure [40,41,42,43,44,45,46,47,48,49]. Despite the good results obtained with different amendments and their relative low cost [50,51,39], these amendments should be carefully selected to avoid potential deleterious effects (i.e. production of secondary waste) that may hinder soil structure and biological activity, and thus, natural soil fertility in the long term [23,52]. Furthermore, weather, contamination depth, soil permeability and potential deep leaching of chemicals also affect the final outcome of the amendment [6]. Utilization of solid bio-waste from local wastewater treatment plants or livestock manure for amending tailings, with high concentrations of HMs, enhancing the properties of the soil to support plant growth for revegetation as well as the recovery of metal from waste, have also been planned by some mining companies in the context of the circular economy [53].

Once these mine soils have been physically and chemically stabilized, the common next step is the successful establishment of a plant cover (Table 1, [62]). Plants favour the ecological development of the ecosystem, enhance fertility of the soil, contribute to the stabilization of soil in open pits and slopes, reduce the HM bioavailability and toxicity, reduce spread of HMs by wind erosion and groundwater leaching and, at the same time, contribute to maintain the aesthetic values of the landscape [45]. The different techniques employed, commonly named as phytoremediation, consist in the use of plants (and their associated microorganisms) to clean up the soil [63,64], through different mechanisms: phytostabilization, phytovolatilization, phytoextraction, phytoexclusion and/or rhizofiltration of HMs (Fig. 2 and Table 1). The application of HM phytoremediation techniques requires the preliminary selection of plant species which are adapted to the local soil and climate conditions and show specific abilities for each alternative [65,66,67,68,69,70]. Ideally, they should tolerate high HM concentrations and extreme salinity and/or pH values, and they should show fast growth rates and/or high biomass production. Thus, metalliferous autochthonous plant species are a common choice because of their tolerance to local environmental conditions and their favourable growth capacities [71]. When using phytoextraction, the selection of plant species that can accumulate high concentrations of HMs in their above-ground tissues, the so-called hyper-accumulators, may be an option [72,73], although limitations derived from their reduced biomass, shallow root systems or their adaptation to the harsh conditions of the mine soil may hinder their application in field conditions [65]. The minimum concentration of a trace element that a plant must contain in its dry weight foliar tissue to be considered as a hyper-accumulator is: 100 mg kg⁻¹ for Cd, thallium (Tl) or Se; >300 mg kg⁻¹ for Co, Cu or Cr; >1000 mg kg⁻¹ for Ni, As, Pb or rare earth elements; >3000 mg kg⁻¹ for Zn or > 10,000 mg kg⁻¹ for Mn [73]. Conversely, in other phytotechnologies, such as phytostabilization or phytoexclusion (Fig. 2), plants that exclude HMs are desirable (see below).

Improvement in plant growth can be achieved through genetic engineering (although using transgenic plants is not universally allowed), or through the addition of certain amendments or soil microorganisms. The exploitation of microorganisms, by themselves or in combination with plants, to sequester, precipitate, or change the oxidation state of numerous HMs has been widely studied [74,75,57,76]. Microbes, mediators of biochemical cycling [77], influence metal speciation and transport in the environment, interacting with metals in reduction, oxidation, methylation and also alkylation reactions such as biosorption, complexation, and mineralization. Microorganisms can sequester toxic metals in their cell wall components or in metal binding proteins, transforming them into innocuous or less toxic compound forms (i.e. less bioavailable). However, they may produce the opposite effect, by releasing organic acids to the soil and the solubility of the metals may increase. Therefore, the application of microorganisms should be carefully evaluated in advance to avoid undesirable consequences. Plant growth promoting rhizobacteria (PGPR) and/or arbuscular mycorrhizal fungi (AMF) have been found to facilitate the accumulation of HMs in plant biomass, to enhance the root structure (higher surface and depth) and their acquisition of nutrients and water, and to increase plant tolerance to acidic pH [78,79,76,80,81]. They may also serve as a filtration barrier to avoid the transfer of HMs to above-ground vegetal parts [82]. AMF, mainly species belonging to the *Glomerales*, and some from the *Paraglomerales* and *Diversisporales*, have been identified in highly contaminated soil (containing 97, 333 mg kg⁻¹ total of Zn and 31,333 mg kg⁻¹ total of Pb), suggesting that these microorganisms are highly tolerant to HMs, which encourages their utilization in HM bioremediation in combination with plants [83]. It has also been reported that glomalin and other glycoproteins released by some species of AMF, besides metal immobilization, may also improve soil stability against wind and water erosion [84,85]. More recently, plants and their associated microbiota have been described as a supra-organisms; holobionts [86]. These holobionts exchange signals to respond to external inputs. In the phytoremediation context, it has been demonstrated that certain plant species (e.g. *Imperata cylindrica*) inhibit the oxidization process of HMs-containing sulphides by limiting the number of bacteria capable of oxidizing Fe and sulphur (S) [87].

2.1. Environmental management in active and abandoned mines

Current mining operations in most developed countries are carried out under strict regulations which, in principle, guarantee adequate mining methods and simultaneous remediating activities [88,62]. Increasing concerns and laws about environmental safety have resulted in more detailed information about relevant mining-related operational aspects becoming available, including the

potential environmental, social and economic impacts, and the activities proposed to mitigate them. In general, the policies of mining companies are aligned with sustainable development principles and include actions to manage and rehabilitate the impact on the mining site as well as its area of influence. These actions incorporate the constant monitoring of potential risks for soil, air and water, and the implementation of active strategies to minimize environmental impact. It has been accepted that a combination of physical containment, chemical/biological amendments and phytoremediation strategies are the best way to remediate mine soil (ITRC, 2009). These techniques are currently being applied by large mining companies to carry out preventative and corrective activities to preserve the environment and they are publicly display on their web pages. However, it has been suggested that some of the worst HM pollution problems in the world have resulted from small-scale operations (e.g. artisanal mining) where all these environmental safety regulations are not being completely fulfilled [89].

Regarding rehabilitation projects, as mentioned above, they are normally enforced or carried out by governmental departments in different countries. There are several examples that illustrate the successful implementation of the techniques indicated above.

2.1.1. US superfunds, United States of America

The US Congress established in 1980 the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), which is informally called *Superfund*, that allows the Environmental Protection Agency (EPA) to clean up contaminated sites (with private or public funds). Thousands of contaminated sites, including manufacturing facilities, processing plants, landfills and mining sites are included in this Superfund (<https://www.epa.gov/superfund/what-superfund>). One of these sites is the *Formosa Mine* (Oregon, US), where the extraction activity of silver, copper and gold stopped in 1993 and the mine ($\approx 300.000\text{ m}^2$ of land) was abandoned. The oxidation of metal sulphides discarded on the surface caused serious acidification of water ($\text{pH}_{\text{H}_2\text{O}}$ 2.44) and soil (pH 3.7). The *Formosa* soil had high concentrations of Cd, Cu, Ni, and Zn [90,91]. The remedy actions designed by EPA include excavating mine impacted materials, building an on-site containment facility to prevent leaching during rain and snowmelt events, paving roads and contouring selected areas to direct water away from the mine waste. In addition, in some areas, a cover of clean materials or a cap was planned to be added, without excavating the waste (<https://cumulis.epa.gov/supercpad/cursites/csitinfo.cfm?id=1002616>). It was demonstrated, with greenhouse pot experiments using mine soil, that amendments with biochar produced from Kentucky bluegrass seed screenings (at $\geq 1\%$) and, with gasified biochar produced with mixed conifer wood logging residues (at $\geq 2\%$) increased wheat (*Triticum aestivum* L. 'Madsen') germination, while in soil without amendments only 30% of wheat seeds germinated [91]. Application of biochar from *Miscanthus giganteus* or lime, assayed using spoils from this mine, indicated that pH and EC values increased in both treatments when compared with control without amendment. Greater β -glucosidase activity occurred only in the 5% biochar plus lime treatment, whilst the *N*-acetyl- β -*D*-glucosaminidase activities were not altered. Lime additions significantly reduced extractable metal concentrations. Increasing biochar rates alone significantly reduced leachate DOC concentrations, and subsequently reduced leachable metal concentrations. *Miscanthus* biochar, by itself, was limited at mitigation, but when combined with lime, the combination was capable of further reducing extractable metal concentrations and improving β -glucosidase [92].

The Iron King Mine (Arizona, USA) was listed on the *Superfund* in 2008 (<https://cumulis.epa.gov/supercpad/CurSites/csitinfo.cfm?id=0905049&mspp=med>). The former operations of the Iron King Mine (Zn, Ag, Pb and Au) and the associated Humboldt Smelter, left behind a pile of about four million cubic yards of orange mine tailings with high levels of As and Pb and large piles of waste and soil contaminated with Pb and other metals. Tailings from the Iron King Mine and Humboldt Smelter mixed together and flowed toward the Agua Fria River and tailings dust has spread into the surrounding area. Tailings and sediment from the mountains continue to move with storm water. The priority remedy action was to clean up in the residential areas. Afterwards, a soil/gravel/rock cap (15–90 cm) was emplaced to be vegetated. Direct soil phytostabilization (vegetable cap using native plants) was also explored [93]. Six plant species, previously shown to either grow successfully in desert mine tailings or at the elevation and climate conditions at the Iron King Mine area, representing drought and salt-tolerant native species of the Sonoran-Arizona desert ecosystem, and belonging to three different functional groups: trees (mesquite [*Prosopis juliflora*], and cat claw acacia [*Acacia greggii*]), shrubs (quailbush [*Atriplex lentiformis*], and mountain mahogany [*Cercocarpus montanus*]) and grasses (buffalo grass [*Buchloe dactyloides*], and arizona fescue [*Festuca arizonica*]) were evaluated for their potential in phytostabilization of HMs with compost amendments; buffalo grass, mesquite and catclaw acacia showed good growth and minimal shoot accumulation of HMs. Researchers found a correlation of plant biomass with increases in soil pH and in the number of neutrophilic heterotrophic bacterial counts, detecting a decreased in iron oxidizer counts and decreased bioavailability of metal (loid)s, mainly as a result of compost amendment [94]. The canopy coverage of tailings amended with compost and seeded with a mix of the six native plants, evaluated previously by Ref. [94]; after 41 months, was from 21% to 61% in the compost-amended planted treatments while no plants grew on unamended tailings [93]. It was also demonstrated that the main chemical driver of microbial diversity during assisted phytostabilization of tailings from the Iron King Mine, in mesocosms, was the pH, with cobalt (Co) being another element highly significant for microorganisms [95]. Cobalt is an important metal in coenzyme cobalamin synthesis, but it can also be toxic to microbial communities. It has been reported that Co potentially inhibits microbially-mediated sulphate reduction in metal-contaminated environments by outcompeting Fe during the synthesis of metallo-proteins. As sulphate reduction processes could mitigate the acidification of mine tailing systems by preventing the generation of AMD [96], demonstrating that Co is one of the main drivers of microbial diversity and that is an important step toward the understanding of the mechanisms behind the efficiency of phytoremediation. Other factors that control the plant-microbe associations during phytostabilization of acidic mine tailings were also explored using buffalo grass grown in unamended vs compost-amended (10%) mine tailings. These results showed an association between domain-level bacterial root colonization and either external substrate or plant condition [97]. Finally, measurements of horizontal dust flux after phytoremediation revealed that vegetated cover enabled an average reduction in dust deposition in comparison to the control treatment. Further, phytoremediation was effective at

reducing the concentration of fine particulates, which represent the greatest health risks and the greatest potential for long-distance transport [98].

2.1.2. The Iberian Pyrite Belt (IPB), Portugal and Spain

This area has been intensively exploited during and after the second half of the 19th century. Large volumes of polymetallic sulfide ore were extracted in open pits or in underground work, processed without any environmental concerns, generating waste rocks and tailings that were deposited in the area, mainly through water erosion and aeolian dispersion. Two examples in the Portuguese sector of the IPB are included in this review. The *Aljustrell mine* was abandoned in 1980 and the main remediation actions consisted in using construction techniques to dig and contain the contaminated tailings and other waste materials, but the remaining soil still needs to be treated [99]. Several studies to assess the possibility of implementing phytoremediation strategies in this area have been published. Although soil from the Aljustrell mine, with a $\text{pH}_{\text{H}_2\text{O}} = 3.6$, contained total concentrations for Cu, Pb and Zn that exceed the overall concentrations for uncontaminated soils. The bioavailable fraction was shown to be very small, both for the mobile fraction and for the mobilizable fraction. However, using a battery of toxicity tests, the authors concluded that the mine soil had a toxic impact on the environment; i. e., *Lepidium sativum* L. (cress) growth was impaired at 40% (v/v) soil concentration compared with the control without mine soil; earthworm *Eisenia fetida* avoided the mine soil at 50% (v/v) and immobilization assays with *Daphnia magna* indicated the sensibility of these organisms to soil from this area [100]. Other studies, carried out with an autochthonal aromatic bush (*Cistus ladanifer* L.), demonstrated that this plant was able to survive and grow in soil with high concentrations of toxic HMs and to accumulate Mn, whilst avoiding Cu and Pb uptake, being classified as an excluder for both metals [101]. Using other autochthonous dominant plant species of the Aljustrell area: *Pinus pinaster* Aiton, *Quercus rotundifolia* Lam., *Agrostis* sp., *Juncus conglomeratus* L. and *Juncus effusus* L., it was demonstrated that the plants were heavily contaminated with Cu, Pb, As and Zn. However, these plants exhibited features of metal tolerant excluders; i.e. the trees were accumulators of Ag, whereas the graminoids were hyper-accumulators of Ag and *Juncus effusus* of Co. The translocation factor confirmed that the selected elements are immobilized in the roots except for Mn and Zn in *Pinus pinaster* and Mn in *Quercus rotundifolia* and *Juncus conglomeratus* [102]. Amendments such as municipal solid waste compost (MSWC), a garden waste compost (GWC) and liming materials, applied to soils from the Aljustrell mine, corrected the soil acidity, increased soil organic matter, available P and K levels and total N, facilitating the establishment of the plant cover with rye grass (*Lolium perenne* L.). All these factors contributed to the immobilization of the Cu and Zn in soil [103]. A semi-field experiment confirmed the good results of the soil amendments with mixed municipal solid waste compost (MMSWC) or GWC, combined with mineral fertilizers and liming materials, on soil properties and demonstrated that *Agrostis tenuis* was a good plant species to be used in phytoremediation as, in general, it did not accumulate HMs in its edible parts [104].

The *Lousal mining* operation, which ceased in 1988, was mostly underground, but it also worked with an open-pit that was partially flooded. Large volumes of waste (estimated in more than 1 Mt) were generated by the mining activities. The water flowing down slope from the waste piles represents a source of AMD into the Corona stream; furthermore, the dam, constructed to avoid the AMD input into the Corona stream, had an infiltration at its base and contaminated the water. The underground connection between the abandoned adits and wells, the ponds and the groundwater spring make this a complex system of 'diffuse' sources of AMD [105,106]. The EDM company (Empresa de Desenvolvimento Mineiro) was responsible for the remediation work at this location within the frame of the rehabilitation programme (RELOUSAL), which was intended to give a cultural and touristic potential to the project (http://www.esga.org/fileadmin/sga/newsletter/news31/SGANews_31.pdf). Therefore, the strategy aimed to confine the environmental toxic elements without significantly affecting the landscape, preserving the visual memory of the mining activities. Physical containment and revegetation were included in the remediation plans, to reinforce the topsoil and reduce soil erosion and water loss by evaporation. Some soil-covered impermeable capping was applied into localized areas to avoid the direct exposure of metal-rich or acid producing solid wastes to rainwater and superficial weathering. Some trenches and culverts, and evaporation ponds were constructed. A wetland system, composed of seventeen "pools", was built between the groundwater spring and the Corona stream in order to minimize the complex problem of AMD. Two different groups of pools, one group with an aerobic environment used for iron precipitation, and a second one designed to favour the precipitation of heavy metals in an anaerobic environment were also constructed. Studies carried out in 2012, in farms and gardens near Lousal mine, showed that, although the levels of As, Cu, Pb and Zn in soils were relatively high, their levels in lettuce (*Lactuca sativa*), coriander (*Coriandrum sativum*), and cabbage (*Brassica oleracea*) could be considered non-toxic. Being cultivated soils, they had been treated with manure, which contributed to an overall raise in soil pH. The conclusion of this study is that gardeners or farm owners near abandoned mines, should be recommended to amend the soil with some liming material, to avoid metal uptake by plants [107].

2.1.3. Cartagena-La Unión mining district, south-eastern Spain

This was one of the most important mining sites for Fe, Pb and Zn on western Europe that was closed in 1991. This semi-arid area was seriously affected during mining activity, and after more than 20 years. Waste from the tailings is still a source of HMs (mainly As, Cd, Cu, Pb and Zn) transfer to the surrounding areas through wind and water erosion [108,109,110,111]. In this case, the removal of waste for disposal was economically unviable and technically difficult. Therefore, in 1982, the mining company Peñarroya SA, sealed the mining tailings with a soil layer 0.5-m thick to allow the colonization of plants. However, the spread of wild plant communities colonizing mining tailings at the "Sierra Minera" is slow [71]. Analysis carried out thirty years after restoration showed that the levels of Cd and Zn in some of the most abundant and representative plant species in the area, including herbs (*Teucrium capitatum*, *Helichrysum stoechas*, *Hyparrhenia hirta*, and *Dittrichia visco*), bushes (*Helianthemum syriacum* and *Thymelaea hirsuta*) and trees species (*Acacia retinoides*, *Pinus halepensis*, and *Tetraclinis articulata*) were excessively high, indicating that the topsoil of restored areas in this mine had not become unpolluted [109]. Laboratory works suggested that the addition of a mixture of pig manure with lime was able to

accelerate the process of establishment of a plant cover in these HM-rich mining soils [112]. In other studies, the halophytic shrub *Atriplex halimus* L. was used in combination with compost (application rate 60 t ha⁻¹) or pig slurry (application rate 60 m³ ha⁻¹) applied as soil surface amendments [113]. The amendments by themselves did not produce a significant direct effect on the solubility of the HMs, probably because the pH remained unaltered after their application. However, the enhancement of the properties of the soil (mainly the increase of soil nutrients and organic matter) favored the development of stable microbial communities and a *A. halimus* cover, and supposed a significant improvement in the stabilization of the soil, minimizing erosion, a real challenging task of stabilizing contaminated soil in semi-arid areas [25]. The plant cover favored the HMs immobilization in the soil reducing their accumulation in the above-ground plant parts.

2.1.4. Gold mining site, South Africa

This mine is the source of several environmental challenges such as AMD and the release of toxic HMs from the tailing sediments. The concentration of various metals varies from 860.3 to 862.6 mg kg⁻¹ for Cr; 324.9–328.4 mg kg⁻¹ for Al; 200.9–203.4 mg kg⁻¹ for As; 130.1–136.2 mg kg⁻¹ for Fe; 121.9–125.8 mg kg⁻¹ for Pb; 27.3–30.2 mg kg⁻¹ for Co; 23.8–26.8 mg kg⁻¹ for Ni; 7.2–9.2 mg kg⁻¹ for Ti; 7.1–9.2 mg kg⁻¹ for Cd; 4.0–5.6 mg kg⁻¹ for Zn and 0.1–0.6 mg kg⁻¹ for Cu. Moreover, the soil was highly acidic (pH = 3.86 to 4.34) with a low cation exchange capacity. Agricultural activities were not supported within the vicinity of the tailings dump on account of the pH level and HM concentration which may impair the uptake of major nutrients by plants [114,115]. The remedy actions consisted in the utilization of the indigenous grass species *Hyparrhenia hirta* as a phytoremediator for *in situ* rehabilitation of polluted soil. This invasive plant species is a tufted and wiry perennial grass with a deep root system [114,115]. This species is often used for soil stabilization as it is known to possess self-fertile and drought resistant potentials for surviving under harsh conditions at mine dump sites. The grass species *H. hirta* was shown to absorb a high total metal mean concentration (4023.67 mg kg⁻¹). Data of uptake for individual metals was as follows: 46.10 mg kg⁻¹ for Cu; 40.08 mg kg⁻¹ for Zn; 859.12 mg kg⁻¹ for Pb; 618.26 mg kg⁻¹ for Cr; 151.70 mg kg⁻¹ for Co and 2308.41 mg kg⁻¹ for Ni. Despite the acidic conditions, the HMs occurring in the soils assayed were successfully absorbed by *H. hirta* grass species [115].

Although these are only a few examples of what have been done in the rehabilitation of abandoned mines, they allow us to confirm that the sealing of the mining contaminated soils with some physical barriers in combination with assisted-phytoremediation is a good strategy for the rehabilitation of mine areas. The application of organic and/or inorganic amendments or the utilization of microorganisms to improve soil conditions and to reduce the bioavailability of HMs is often needed to first prepare the soil from abandoned mining areas for further actions such as the establishment of the plant cover [78,116,117,76,118,119,47]. Plant species to be used (hyperaccumulators, excluders or well-adapted plants to the area conditions) should be carefully selected to maximize the benefits.

2.2. Tailing dam failures case studies

The failure of tailing dams has provoked some of the main environmental disasters of the last decades. The consequences of these occasional and unexpected contaminating episodes may well be more serious than other sources of HM pollution. Although there is no complete inventory of tailing dams, it is estimated that there are around 2,000–3,500 active tailings impoundments around the world [120], and it is assumed that 2 to 5 “major” and 35 “minor” tailing dam failures would occur on average per year [121,122]. In total, more than 200 mine waste dam incidents have been reported throughout the world since 1960 [123,124] <https://www.wise-uranium.org/mdaf.html>; <https://www.resolutionmineeis.us/sites/default/files/references/bowker-2019.pdf>).

Tailing dam failures obviously cause injury to people and loss of infrastructures, but they also provoke an increase in turbidity of the water (most of the tailings spilled into rivers) with concomitant increase in HM concentrations in the nearby water and soil [125, 126,127], and immediate toxicity for aquatic organisms, insects, and plants as well as medium- and long-term toxic effects. Bioaccumulation of HMs in algae and plants has been reported, with this accumulation, as indicated above, being one of the main entries of HMs to the food web [128]. High sulphate levels in freshwater cause salinization, which leads to a decrease in dissolved oxygen with potentially lethal effects on aquatic species as a result of osmoregulatory stress [129,130]. Modifications in the microbiota are also common in these spills; increases in the number of Fe-tolerant microorganisms were observed after the tailing dam failures Córrego de Feijão and Germano mines in Brazil [131,127]. The metabolic potential of the bacterial communities was altered in contaminated water after the Mont Polley mine accident, increasing the number of bacteria mainly involved in the cycling of S and metals, whilst that of the communities in undisturbed areas were associated with the cycling of N [132].

To illustrate the effect of tailing dam failures on agricultural land and how the restoration of the land has been or is being achieved, we have selected three different cases in Asia, Europe and South America with around 20 years of difference between them, to comment on the advances produced in the management of these serious accidents. The World Mine Tailings Failures database (<https://worldminetailingsfailures.org/>) set a four-level severity code for mine tailing failures that is based on several variables, including the volume of released material, runoff and deaths. The accidents selected here have been classified as very serious (level 1).

2.2.1. The Xingping mine, Guangxi region (China), 1976

In the Guilin region of Guangxi Province (South China), the tailing dam of the Pb/Zn Xingping mine (active from 1950 to 2012) collapsed in 1976 after a heavy rainfall, which lasted three days. Most of the mineral processing wastewater, which had accumulated in a single tailing pool, with no treatment, reached the nearby side stream and, consequently, the large agricultural area of the village, located 6 km away from the tailing pool and connected with this stream for irrigation purposes. Because of the land orography and properties, this HM-containing wastewater persisted in the agricultural soil for a long time after the flood receded, resulting in a large-scale soil pollution event [133]. The mean concentrations detected in the topsoil in 1986 of Zn (3936 mg kg⁻¹), Pb (2007 mg kg⁻¹), Cu

(239 mg kg⁻¹), and Cd (14 mg kg⁻¹), were much higher than the national standard values of 200, 50, 50, and 0.3 mg kg⁻¹, respectively [134].

In the first years after the accident, “remedial measures” were adopted by the local residents; deep soil, probably unaffected by the pollution, was excavated and relocated on the surface, whilst the polluted sludge was buried at the sub-surface [133]. From 1976 to 1986, other remediation actions were undertaken, including cementing the river channel, mixing contaminated soil with allochthonous non-contaminated soil, cultivating non-food crops, and adding lime and fertilizers to the polluted soil. Since 1986 to 2015, the application of lime and fertilizers and the cultivation of non-food crops, were the strategies used to decrease metal levels in the soil and the agricultural land was transformed into orchards [134]. In 2015, the Zn, Pb, Cu and Cd content of topsoil of the nearby village, evaluated by Ref. [134]; had significantly decreased when compared with the HM content in 1986, but still remained higher than the Chinese National Standards; with Cd being the priority contaminant when measuring available concentrations or ecological risks [134].

In 2016, a Chinese company (Beijing Ruimeide Environmental Remediation Co. LTD.) was commissioned to perform remediation labours in the polluted area. The first approach was focused on increasing the solubility of the metals in the soil and the bioavailability of metals to plants by adding citric acid (activator), to favour subsequent phytoextraction activities [135]. The phytoextraction was carried out by planting *Amaranthus hypochondriacus* just after the application of the amendment. This plant species is a fast-growing and easily cultivated plant, which can accumulate over 100 mg kg⁻¹ of Cd in the shoots [136]. A second type of chemical amendment was intended to stabilize the HMs in the soil (e.g. adding calcium phosphate, a passivate), to alleviate their toxicity to plants. Li and co-workers (2020), studied the effectiveness of these treatments using soils with different degrees of HM contamination. Several physiological parameters in pakchoi (*Brassica campestris* L. ssp. *Chinensis* Makino) such as seed germination, plant growth properties and HM accumulation, were analysed two years after the treatment (in 2018). No effects were detected in seed germination when using soil with different concentrations of HMs with or without chemical amendments. However, certain growth parameters and values of HM concentration in the biomass had increased when calcium phosphate was used as an HM immobilizing agent. Although to a lesser extent, the use of an amendment based on citric acid also resulted in satisfactory pakchoi growth parameters and HM extraction rate [137]. In the case of highly polluted soil with no chemical amendment, the development of pakchoi plants turned out to be non-viable [137]. In all the cases the concentration of HMs in pakchoi exceeded the threshold established in the national regulations for food safety (GB2762-2017). Therefore, when using pakchoi or any other plant species at field level for the phytoextraction of HMs, the resultant biomass should be subjected to strict monitoring and suitable management depending on metal levels detected. In this case, an incineration station for the appropriate treatment of resulting biomass was established near the remediated area [137].

Despite these remediation efforts, in 2018, the total levels of Pb, Zn, Cd, Mn and Cu, were still higher than the national standards for soil quality; whilst the potential ecological risk was almost negligible for Zn, Mn and Cu, but still high for Pb and Cd [133]. These studies also revealed that soil pH increased after the accident, a result that differs from the disturbances observed in other Pb/Zn mines [138,139]; this is probably due to the inherent properties of the soil in the area enriched in calcium (Ca), and poor in S [133]. The pollution gradient was found to affect soil microbial properties, such as soil enzymatic activity: catalase, protease, invertase and urease activities were lower in the samples with higher level of HMs [133].

The final conclusion of these studies is that, despite the remediation efforts, though it has been 40 years since the incident, the HM levels in soils are still not safe for agricultural practices [134,137,133].

2.2.2. The Aznalcóllar mining site, Sevilla-Huelva (Spain), 1998

A toxic spill, at the time the largest in European mining history [140], occurred in the Aznalcóllar mine complex, south-western Spain, in late April 1998. The pond, containing saturated pyritic tailings, released around 6×10^6 m³ of sludge and acidic water with a high HM content [141]. In the first hours, more than 4000 ha, comprising alluvial soils of the Agrio and Guadiamar river valleys, were covered by a layer of variable thickness (over 30 cm in some points) of black sludge [142]. The HM contaminant history and remediation efforts in this incident have been extensively reported [143,144,145]. Besides the socio-economic consequences, the main environmental impact in the affected area consisted of the acute increase of HM concentration (Zn, Pb, Cu, As, Sb, Bi, Cd and Tl), and a decrease of pH [146]. The initial impact of the sludge was not uniform in the affected area but depended on several soil characteristics (e.g., texture), which differed from some sites to others. Within the first days after the accident, the rapid changes in the water flow surrounding the pond provoked the death of most aquatic animals as well as other amphibians, birds, and mammals living in the vicinity [141].

Remedial actions were carefully planned and carried out in different phases. Emergency actions, deployed immediately after the accident, consisted of a soil clean-up, where $6\text{--}10 \times 10^6$ m³ of sludge together with, at least, 10 cm of the top soil layer were removed to an open-pit mine. These first operations had an estimated cost of 170 million euros [147]. In a second phase, an intervention was required to neutralize the acidity [148,149] and therefore, inorganic (e.g. CaCO₃-rich substrates such as sugar beet lime) and/or organic amendments (e.g. compost, leonardite, which is rich in aromatic and lignin-derived compounds) were applied in accessible areas. In general, the amendments provoked a rapid pH increase, which induced a reduction in the available HM concentrations and consequently, avoided the dispersion in acid/acidified soils, where the oxidation of metal sulphides could have facilitated the potential leaching of HMs to deeper layers [150,118]. Despite the improvement in soil properties (higher pH, increased organic carbon content and decreased bioavailability of HMs), which facilitated the establishment of a remarkable plant cover, the HM concentration in these soils was still over that in the non-affected areas [151]. Consequently, a periodical application of the same or other amendments was recommended to enhance the remedial process [152]; p.; [118,153]. The information obtained from the management of this spill has emphasised the importance of a careful management of the amendments applied to avoid undesired effects; e.g. an excessive pH increase when liming could reduce the ability of CaCO₃ to react with acidic components, or the uncontrolled increase of organic matter

in soil may enhance the transfer of elements such as antimony (Sb) to plants [154,155].

In a last stage, phytoremediation approaches were applied, reforesting most of the contaminated area with different plant species [156]. Phytoextraction assays were carried out in experimental plots using several plant species, mainly belonging to the family *Brassicaceae* (*Brassica napus*, *B. carinata*, and *B. juncea*), selected for their notable capacity to accumulate HMs [157,113,158]. However, in the best-case scenario, the HM removal rates turned out to be from low to moderate, making this approach impracticable for large areas with high HM concentrations [157]. Although adding chelators (e.g. NTA, nitrilotriacetic acid or EDTA) to the soil was demonstrated to enhance HM phytoextraction, this practice was ruled out since most chelating compounds are known to be toxic and non-biodegradable [159]. The results of the phytostabilization experiments, based on the establishment of trees (e.g. *Quercus ilex* and *Olea europaea*), shrubs (e.g. *Retama sphaerocarpa* and *Myrtus communis*) and herbaceous species (e.g. *Lupinus albus*), showed that the transfer of HMs to above ground tissues and improvements in soil structure were greater with trees and shrubs than when using herbaceous plants [160,161,162,68]. Amongst the assayed shrubs, *Retama sphaerocarpa* showed higher rates of survival and retention of HMs compared to other shrubs such as *Myrtus communis* or *Rosmarinus officinalis* [163,161,164]; p.). In the case of herbaceous species, white lupin (*Lupinus albus*) was also identified as a good candidate for HM stabilization due to its high HM retention rates and its capacity to increase soil pH (Vázquez et al., 2006). These plant species may also have a role as nurse plants by facilitating the establishment of seedlings of other late-successional species (e.g. oaks) through the amelioration of extreme microclimatic conditions [161,165]. The possible contamination effect on soils by biomass litter enriched in HMs was also analysed. In the case of poplar litter, the HM concentration in soil did not increase significantly, and thus, the plant growth was not negatively affected [166,167]. Conversely, this litter provided organic matter to the soil which, in turn, induced the amelioration of other parameters such as soil pH [167,168].

Permanent monitoring actions have been put in place to follow the evolution of the contamination. In the first months after the spill, non-remediated areas suffered a progressive acidification process linked to the weathering of carbonates and the mobilization of certain HMs to deeper substrates [156]. In the case of river banks and beds, the bad accessibility limited the application of adequate remediation actions; thus, the risks related to the spread of mobile elements such as Cd and Zn remained unmanageable in these habitats [169]. In the affected area, after the sludge removal, most soils presented HM levels higher than those soils unaltered in the Guadiamar valley [161]. Determinations made almost 40 months after the accident (in 2002) found concentrations of Hg in the soil surface (0–5 cm) more than 8 times higher than the background value of the area, although this concentration was very variable along the Guadiamar river basin [170]. Through monitoring analyses, high levels of HMs were also detected in native plant species (*Cynodon dactylon* and *Sorghum halepense*) growing in remediated and non-remediated plots, [171]. Overall, 15 years after the accident, and despite remediation efforts, about 7% of the surface within the first 18 km of the polluted area were still bare soils [169,172]. In some spots, the concentration of certain HMs was even higher than before the restoration work; this effect was attributed to the soil compaction effect caused by the heavy machinery removing sludge as the first remedial action [173]. However, mechanical removal of sludge and polluted top soil also accelerated the natural attenuation in other areas [118]. The utilization of plants as bio-indicators of pollution was also studied; thus, the content of HMs on leaves of white poplars (*Populus alba*) was found to fit well with the availability of certain HMs in soil [174]. Similarly, *Eucalyptus camaldulensis* was shown to be a good biomonitor for Cd, Mn, and Zn in soil [162]. The plant-monitoring results confirmed that the presence of HMs in plants had decreased after the remediation efforts (12 years after the accident), reaching levels that could be considered normal for higher plants and tolerable for livestock [156]. In combination with these control measures, several alternative uses, such as the production of biofuel or the use for horse grazing (non-food livestock), were proposed and tested to take advantage of the HM enriched biomass produced in the contaminated site [175,176].

Overall, a progressive recovery of the ecosystem functions altered during the pollution episode was observed; enzymatic activities that were affected in contaminated areas, or indices such as microbial biomass carbon or microbial diversity were gradually recovered after remediation [177]; 2010; [152,118]. The regional administration managing the Aznalcóllar situation established a protected area, where certain activities such as agriculture or the collection of terrestrial snails for human consumption were limited or, in some cases, prohibited [144], and currently it is just a recreational area.

2.2.3. The Germano mine, Minas Gerais (Brazil), 2015

The accident at the Germano mine is considered one of the most serious dam failures registered because of the injuries to people, loss of infrastructures and the effect on vegetation and agricultural land (over 2,000 ha were affected). On November 5, 2015 the second of a set of three sequential tailing dams, the Fundação dam, failed and the tailings spilled into the third dam, Santarém, which overflowed with 60 million m³ of water and mud, destroying the town of Bento Rodrigues, and swamped the River Doce. Over the following weeks the mud funnelled the mining waste 650 km into the Atlantic Ocean [131]. The shape of the river changed because of the rapid displacement of the large volume of material in a short period of time.

Although the composition of the tailings was not known in detail, the presence of quartz and toxic chemicals used in reverse cationic flotation, such as ether amine and sodium (Na), was expected because of the Fe-extraction technique used in the mine [178, 145]. After the disaster, Samarco interrupted its activities and the non-profit Renova Foundation was created for managing the restoration and reconstruction programmes of the regions impacted by the disaster with estimated costs of US\$54 billion [179,180].

The immediate impact was similar to other accidents; large depositions of waste along the Doce basin and an increase in suspended sediment loads (up to 33,000 mg L⁻¹). The levels of Fe, As, Hg, Mn exceeded sediment quality guidelines [126]. In the short term (two days after the accident), the pH did not change in the water column [181]. In this accident, the benthic estuarine assemblages were found to have significantly changed, with an increase of metal resistant taxa. Benthic communities are used as environmental markers for monitoring ecosystems, because being mostly sedentary and with short life cycles they are directly impacted by organic and chemical disturbances [181,182].

Measurements carried out one and two years after the accident (in 2016 and 2017), revealed that the riparian soils reached by the sediments showed a reduction in fertility, especially of the content of soil organic matter and NO_3^- (but also due to other elements such as P, K, Ca, Mg, Cu, Fe, Mn, and Zn) with a concomitant increase in NH_4^+ , Na, and pH. Sodium reached values as high as 150 mg kg^{-1} , whilst metal toxicity derived from Fe, Cu, Mn, and Zn was not observed. Ether amines and Na present in the sediments had strong toxic effects that resulted in the depletion of total microbial biomass (measured as phospholipid fatty-acid content) and overall plant mortality in the impacted zone [183]. The short-term impact on microbial communities (analysed in 2016–2017) included an increase in Actinobacteria and Bacteroidetes and in gene sequences related to microbial virulence, motility, respiration, membrane transport, and Fe and N metabolism, suggesting changes in the microbial metabolic profiles [125].

The long-lasting effects of this accident are still unknown; however, the identification of Na and amines in these sediments will help to design efficient remediation strategies.

Overall, the actuation in these three accidents indicates that the general awareness toward the noxious effects of these environmental disasters have increased with time. The strategies to face this type of situations have been clearly established (removal, mobilization/immobilization of contaminants and phytoremediation) and the monitoring techniques have significantly advanced. However, the techniques applied have not changed much in twenty years, although nowadays it is well established that the amendments, phytoremediation approach etc. Should be determined on the basis of the specific characteristics of the contaminated area and that fast responses should be taken.

3. HM accumulation during agricultural activities and remedial actions

By 2050, the agricultural production at a global level is needed to double for reaching the expected requirements of a growing population [184]. Soil degradation of agricultural areas worldwide is a global threat linked to severe losses in the crop yield, which is especially worrying in the most vulnerable areas on earth, due to the risk of aggravation of poverty and malnutrition [185]. The long-term application of impure inorganic pesticides, fertilizers and/or organic amendments, such as liquid and soil manure, or their derivatives such as compost or sludge, containing relatively high content of metallic elements such as Cd, As, Cu, Zn, Cr, and Pb, has significantly contributed to the progressive HM accumulation in soil [186,187,188,189]. Irrigation of crops with wastewater, rich in C, N or other nutrients, is a common practice in arid or semi-arid areas, which minimizes the need for chemical fertilizers but frequently contributes to the accumulation of HMs in the soil, unless they have been previously treated to remove the metal load [190,191]. In addition, it must be taken into account the enhanced root proliferation, induced by these amendments, which enables plant access to larger pools of bioavailable HMs. Besides the deleterious effects of HMs on plants [18,115], HMs alter key functions in soil, minimizing the availability of nutrients and the biological activity of the soil, impairing soil fertility and crop productivity as well as producing alterations in the microbial community structure [192,193]. International institutions dependant on the United Nations, WHO (World Health Organization) and the FAO (Food and Agriculture Organization), strive to raise worldwide social awareness about this issue by launching actions addressed to prevent further pollution and to minimize the contamination problems in agricultural soil worldwide by using environmentally friendly techniques (UNEP, 2019). Therefore, there is a growing interest in remediation technologies applicable to agricultural soil.

Most of the active remediation/preventive strategies for agricultural soil are comprised in the ecologically sustainable Gentle Remediation Options (GRO). Since the pollution of agricultural soil with HMs are frequently slow progressive processes, these GRO non-aggressive methods might be an efficient and low-cost approach. GRO mainly include the use of organic/inorganic amendments for the *in-situ* metal stabilization/inactivation, the application of selected soil management practices aimed at decreasing the bioavailable HM content, and/or, the use of plants (productive crops and assisting plant species) and their associated microorganisms with phytoremediation purposes [194,195].

The aim of metal stabilization through the application of organic and/or inorganic materials, is to reduce the bioavailability of HMs in the topsoil layer, and thus, the contaminant translocation to plant tissues [196,23]. Some amendments may also provide additional benefits, particularly interesting for agricultural soil, such as the enhancement of soil physic-chemical and biological properties through the increase of porosity, aggregate stability, organic matter content, cation exchange capacity, water-holding capacity, and microbial activity, as well as pH buffering; furthermore, some amendments contain essential nutrients that favour plant development [197,24,59,198,199,200,201,202,203]. The selection of pollutant-excluding crop cultivars to reduce the entry of toxic metals into the human food chain is one of the most widely used agronomical practices applied to metal-impacted soils [204,205,206,207]. This strategy requires the selection and utilization of crops with low HM accumulation in their harvestable tissues. Those excluder cultivars can be obtained by selecting specific phenotypes and incorporating them into plant breeding programmes. Finding low HM accumulation cultivars (LACs) have been investigated mainly with Cd [208,206]. Investigation of LACs in the last twenty years has led to identification of rice, wheat and others plants that accumulate low concentrations of Cd, or rice cultivars with a low accumulation of As or Hg [206]. Decreasing the total HM concentration to below a safe threshold value without compromising crop yields is especially important in developing countries. Intercropping has emerged as an appropriate option; thus, the co-cultivation of hyper-accumulators with crops decreases the uptake of contaminants in crop plants. Furthermore, if the hyper-accumulators are left during the time interval between the first and second cropping seasons, the HM removal will continue. Successive cultivations will progressively eliminate the HM content in the soil [209,210,211,212,213,214]. Nevertheless, it should be noted that the selection of some of these strategies may hinder the agricultural production, either by limiting the cultivation of less valuable crops during long periods of time due to the relatively slow phytoextraction process or limited productivity due to the intercropping strategies [215].

Studies carried out to investigate the HM accumulation capacity of twenty plant species grown in agricultural soil irrigated with wastewater for approximately 60 years, showed a high variation in metal accumulation capacity amongst all vegetables evaluated. For

instance, spinach, Chinese lettuce and Chinese chives showed the highest capacity and thus, the highest health risks. On the contrary, other crops such as tomato, potato or cabbage showed low accumulation values and thus, less health risks despite high soil HM pollution [216]. This study links the necessity of wastewater pre-treatment and a proper crop selection to mitigate the risks for human health when exploiting polluted soil for crop agriculture [216,217].

We have found only two field studies related with remedial actions under real conditions. In the first one, conducted in Sichuan Province, China, during the whole growth stages of rice crops, the authors evaluated the efficiency of eight immobilizing treatments for the remediation of Cd contaminated soils. All amendments, composed of mineral fertilizers and different proportions of synthetic zeolite, led to positive results. The mixture of the mineral fertilizer: synthetic zeolite at mass ratio of 10:6 proved to be the most promising material for remediation of Cd contaminated paddy soil, due to its high efficiency at metal immobilization and pH buffering, as well as being cost-economic [218]. In the second study, the application of amendments was tested in the vicinity of the city of Verdun, in north-eastern France. In the 1920s, 1.5 million chemical shells and 30,000 explosive shells were destroyed nearby causing the release of relevant concentrations of Zn, As, Pb and Cd. The cultivation of wheat, the traditional crop in the area, was stopped because the risk of human exposure to As, via the consumption of wheat derived products [219]. A schwertmannite-based adsorbent material, assayed for treating this soil in pot experiments, induced a reduction of As availability but an increase in that of Cd and Pb. Additional experiments showed that the combination of this substrate with chalk or ash solved this issue by reducing the mobile fraction of As in soil without affecting negatively the Cd and Pb concentrations [220]. These results support the recommendations of combining fertilization and liming for the effective remediation of As-rich soils [221], and the need to carefully analyse potential adverse secondary effects before the large-scale application of amendments.

4. Valorization of the phytoremediation

The final aim of phytoremediation must be to extract or stabilize contaminants in the soil to avoid their mobilization through the trophic chain. In the long-term, it should be pursued to achieve the progressive full recovery of the soil, which would provide environmental, social and economic benefits. One of the main challenges of remedial technologies is the cost of the process, and therefore, it has been proposed that obtaining economic benefits during phytoremediation would attract companies to increase their remediation efforts [222,223,224].

4.1. Phytostabilization and bio-energy production

When plants which have been grown in contaminated fields under remedial treatment cannot be cultivated for crops (i.e. no resistant or LAC crop varieties exist, elevated concentrations of HMs that are transported to the harvestable parts even in LACs), bio-energy crops could be a good option to generate income [225]. As phytoremediation projects often require quite long periods of time to be successfully completed, production of energy crops could pose an attractive economic alternative to local farmers that would allow a sustainable use and valorization of contaminated soil. Experiments carried out in Campine, a HM-contaminated region along the Dutch-Belgian border, have demonstrated that cultivating maize (*Zea mays* L.) resulted in an annual reduction of Zn in the top soil layer of about 0.4–0.7 mg kg⁻¹ (although removal was low for Cd and Pb). Cultivation of non-edible maize could result in 33,000–46,000 kW h of renewable energy (electrical and thermal) per hectare and year which by substitution with fossil energy would imply a reduction of up to 21×10^3 kg ha⁻¹ y⁻¹ CO₂ if used to substitute a coal fed power plant [226]. Similar experiments, but using a short-rotation willow coppice, also showed good removal of HMs. As the plant biomass was able to capture atmospheric carbon at the same time that the soil contamination was being reduced [227], there is a total sustainability of the process. However, the final destiny of the HM in these energy crops as well as the risk of HM transfer to the food web through the wild fauna should be further investigated.

4.2. Phytomining or agromining

Increasing demand for metals has scaled up the metal prices to unsuspected levels. Furthermore, the possession of rentable metal (oid)s deposits is actually a strategic resource for many countries, which causes conflicts in the world (Global Policy Forum; www.globalpolicy.org). In this context, phytomining is an eco-friendly strategy that consists of using plants able to extract valuable elements from the substrate and accumulate them in their above ground tissues from where they can be recovered after biomass processing (bio-ore) (Chaney et al., 1998). In general, phytomining relies upon the availability of plants able to hyper-accumulate the element(s) of interest. Currently, more than 700 H M hyper accumulator plant species have been reported [73], of which most of them accumulate Ni. The criteria for selecting a hyper-accumulator useful for phytomining in contaminated soil is not only about the concentration of the metal in the plant, but also the biomass and growth rate, in order to reach high amounts of the element of interest per hectare [228]. Phytoextraction is only the first step of the whole metal recovery process; further steps, such as plant biomass reduction (for a cost-effective transportation and ulterior manipulation) and metal extraction should be implemented (Table 2; [229, 230,231,232,233,234,235,236,237]). The term agromining considers the entire agrosystem including all the techniques and actors in the chain to obtain elements of interest from metal-rich substrates using plants [238,239]. Agromining has been assessed in soil naturally enriched in Ni (ultramafic soil; see revisions by Refs. [240,241] and can also be implemented to mine slags and sites contaminated with valuable HMs with the double objective of achieving soil restoration whilst obtaining profits from the commercial production of metals [242]. It should be noticed that agromining is an interesting strategy which, in practice, is only economically feasible for certain metals of high economic value that can be phytoextracted in sufficient amounts to compensate for the costs of biomass production and recovery of the element of interest [238]. Elements with high interest of recovery are Cu, Co, Tl and Se and

rare earth elements (REEs), such as neodymium, yttrium, dysprosium, europium and terbium [239], but hyper-accumulators have either been found to grow in very specific locations, or the contaminated soil containing these materials is quite rare. The phytomining of metals such as Ag or Hg is still challenging because of the lack of plants capable of accumulating them. In the case of other phyto-minable elements, such as Cu or Pb, their market value is too low for considering them as potential targets for phytomining [239].

Currently, most of the practical demonstrations of phytoextraction or phytomining of metal (loid)s from contaminated soil are small-scale and short-term trials. Most of these demonstrations have been based on using hyper-accumulator species, such as *Thlaspi caerulescens* (Pb, Zn, Cd, Ni), *Odontarrhena* spp. (Ni, Co), and *Pteris vittata* (As) or fast-growing plants, such as *Salix* and *Populus* spp. that accumulate above-average concentrations of only a small number of the more mobile trace elements (Cd, Zn, B) [243]. The only complete process of agromining in contaminated soil described so far have been the recovery of nickel from brown-field sites [244–247]. It should be considered that agromining is a temporary activity (whilst there are high concentrations of metal in soil), and therefore, its main objective is the improvement of soil quality to allow food crop production whilst obtaining economic benefits [246]. Therefore, there is not competition with food crops for land usage.

5. Future perspectives

A clear challenge in remediation of metals will be the elimination of *emerging inorganic contaminants* [248]. Current production of lithium (Li) is 77,000 tons per year (USGS, 2020), mainly produced for rechargeable batteries. Gallium (Ga) and indium (In) are used extensively in electronic equipment. It has been reported that industrial sludge associated with electronic manufacturing contained up to 40–42 mg kg⁻¹ of In [249]. These three elements are some of the elements that are now being considered as emerging contaminants and are present in waste from electronic industries that have been termed as e-waste. Although not yet studied in depth, phytoremediation could be a good alternative in the remediation of contaminated soil or water, or in the bio-recovery from rich waste material. Li is entering in the food chain through various mechanisms and being taken up by all plants [250,251]. In the case of Ga and In, being chemically similar to aluminum (Al), it is thought that some acidophilic plants, such as *Camellia* spp., which accumulate Al, could also be used for Ga and In accumulation [248]. Further studies in this area to identify the best plant species, or even the microorganisms to be used in wastewater treatment plants, would allow the development of new technologies for the remediation and/or recuperation of these elements.

Nanoremediation has recently emerged as an innovative technology aiming to enhance the efficiency in the immobilization of contaminants (e.g. HMs) from soil and water through the application of, engineered or biogenic, nano-sized materials (NMs) [252]. These materials present some interesting properties, such as high surface-to-volume ratio, low reduction potential, low cost, or potential surface functionalization, which make them versatile and highly reactive entities for selectively remediating pollutants in the environment [253]. The performance of these NMs can be enhanced by modifying the properties of their surface by coating them with biopolymers (e.g. starch or ethylene glycol) or customizing their size, morphology or chemical composition by controlled chemical reactions [253,254,255]; Ingle et al., 2022). Nano-materials can also be generated biogenically (e.g. by plants, bacteria, algae, or fungi). In the field, the application of these NMs can be carried out by distributing them directly onto the polluted site or by creating the precise conditions for the NM formation or activation on site. For the activation of NMs, a common approach is the inoculation of selected microbes by spray irrigation, infiltration galleries, or injection wells if the pollutants are deep in the soil. Once in contact with the contaminant(s), NMs may exert a direct effect on them through adsorption/redox reactions, or indirectly, they can increase the efficiency of other remediation strategies (e.g. phytoremediation) through different mechanisms such as assisting plants to stabilize HMs by electrostatic adsorption or, simply, by stimulating plant growth [256].

So far, numerous types of NMs, mainly nano-particles (NPs), have been investigated for a variety of applications as HM remediation [257], although they have not been thoroughly evaluated under real scenarios. In particular, NMs such as TiO₂-NPs and nano-scale zero-valent iron (nZVI) have been widely investigated for HM remediation purposes [258,259,260,261]. In the case of the NPs of TiO₂, they have been successfully tested for Pb adsorption in soil [262], as well as for enhancing the accumulation of Cd in soybean plants (*Glycine max*). After 60 days in contact with TiO₂-NP, the accumulation of Cd in soybean shoots and roots increased approximately 2–3 times (in comparison to normal accumulation values) depending on the TiO₂-NPs concentration [263]. Regarding nZVI, an electron donor with a negative reduction potential, it has been shown to remediate Cr(VI) and Hg efficiently [264]; [259]. In addition, nZVI also improved the Cd and Pb phytoextraction potential in the roots, stems, and leaves of *Boehmeria nivea* and *Lolium perenne*, respectively [265,266].

Other NMs which have been investigated in this regard are magnetic NPs, whose properties could provide certain advantages in the remediation of metal-polluted soil. Recent studies with biogenic magnetite (Fe₃O₄) NPs confirmed a high potential in the remediation of certain pollutants such as Cr(VI) [267]. In addition, Ag-NPs in combination with PGPR have been reported to modulate the growth and phytoextraction capability of maize plants [268], salicylic acid NPs improved *Isatis cappadocica* phytoremediation in As-polluted soils [269], and MgO-NPs assisted the Pb accumulation in *Raphanus sativus* [270].

To sum up, nanotechnology-based strategies are expected to enhance existing remediation approaches by accelerating the clean-up procedure, reducing economic and environmental costs, and mainly, customizing the process to each particular polluted scenario (reviewed in Shahid et al., 2022) as well as for creating precise agricultural management systems (reviewed in Ref. [271]. However, the environmental consequences of using nano-materials should be carefully evaluated when applying this technology *in-situ* [272].

6. Conclusions

Despite the current trend to develop sustainable mining and agricultural practices, HM contamination of soils is still a huge problem affecting soil health. Although ecosystems are known to have great resilience to external alterations, the natural attenuation processes are usually very slow [273]; therefore, implementing environmentally sustainable remediation strategies for soil affected with high concentrations of HMs is still a necessity.

All the examples summarized here reveal the complexity of using standard protocols for the remediation of soils contaminated with HMs. In highly contaminated environments, usually related to mining sites, and if economic constraints allow it, physical containment in combination with assisted-phytoremediation have been demonstrated to be the best approach for environmental restoration. Difficulties associated with the topography of these mining areas, the vast area to be remediated, economic constraints, and, sometimes, the need to take urgent decisions (i.e. after spills), have made difficult the field application of some of the innovative remedial techniques that have shown good results in the laboratory after huge research efforts.

In agricultural soils, the problem of HM contamination has been only recently acknowledged, and thus, the optimal management and remedial strategies are still being investigated. So far, several approaches have been tested and discussed. In the case that agricultural exploitation must be preserved during remediation actions, an approach combining different management and treatment possibilities is expected to reduce risks for a safe use of polluted agricultural lands. Nevertheless, in all cases, a constant ecotoxicological monitoring programme is essential, and cultivation should not be allowed unless intensive and periodic toxicity tests demonstrate the safety of the crops for consumption.

Further research is clearly necessary to optimize the existing remedial approaches by reducing their duration and enhancing their applicability, as well as implementing new efficient and cost-effective treatments such as promising nanotechnology-based methods. These promising innovative approaches, successfully tested at laboratory level, need to be validated in the field to make them effectively applicable (from a technical and economical point of view) in the medium and long term. Phytomining or the use of biomass from phytoremediated areas for bio-energy production could help to support the costs of the remediation, however, none of these options have so far been extensively used or developed by industry.

Author contribution statement

All authors listed have significantly contributed to the development and the writing of this article.

Data availability statement

No data was used for the research described in the article.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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