Chapter 1
Phytoremediation of Mining Areas: An Overview of Application in Lead- and Zinc-Contaminated Soils

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1.1 Introduction

The metals concentration in soils is connected with natural and anthropogenic factors: metals are naturally present in soil in trace as a consequence of the decomposition of pedogenic substrate, while, anthropogenic activities such as emissions from the industrial areas, mine tailings, disposal of wastes, wastewater treatment, land fertilization and animal manures entail the release of metals into the environment, a large proportion of which are accumulated in soil [1–3]. On the basis of data reported by UNEP [4], mining is a significant contributor to the national economy in 158 countries worldwide.

Processing of lead and zinc metallic ores may involve a number of physical and chemical steps in order to separate the mineral resources from the less valuable material (gangue) [4]. Profitable recovery of lead and zinc ranges from about 3 % of metal in ore, for large and easily accessed mines, to more than 10 % in case of extremely costly and remote mines [5]. Minerals process, usually, produces several environmental impacts linked to each different stages of the process and generates large volumes of waste. Especially, waste rock and tailings represent a secondary source of pollutants that could contaminate soil, surface water and ground water even for hundreds of years after the mine closure. Moreover, the extent of contamination

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due to the mobilization of metals can interest areas of hundreds of kilometres away from historical mining sites depending on site characteristics [6, 7].

Metals are included in lists of priority pollutants of US Environmental Protection Agency (Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl and Zn) and of European Union with the Directive 2013/39/EU (Cd, Hg, Ni and Pb). These lists include both essential elements, toxic depending on the dose (e.g. Cr, Cu, Zn), and non-essential toxic elements, e.g. Hg and Pb [2, 8]. Different approaches can be considered for soil remediation: isolation, immobilization, toxicity reduction, physical separation and extraction. The selection of the most appropriate method depends on the site characteristics, nature of pollutants and their concentration. Physical and chemical technologies are well known and extensively applied [9], but can alter soil and landscape characteristics and entail high costs due to the wide areas involved [10–12]. Conversely, phytoremediation has been universally considered as a cost-effective technique that permits to restore biological activity and physical structure of soil (among others, [13–17]).

1.2 Lead and Zinc Mining Worldwide and Related Environmental Impacts

Mining activities produce several environmental impacts linked to each different stages of the mineral exploitation: starting from the exploration for the discovery of mineral deposits, the ore extraction and mineral processing until the mining closure and remediation of the site (Table 1.1).

The extent of impacts caused by mineral exploitation depends on site characteristics, amount of material handled, chemical composition of ore and surrounding rocks, extraction processes and technologies used to prevent or reduce the effects [4]. The excavation and the removal of vegetation related to exploration and operational phase are associated with metals contamination and erosion of soil [5]. The mineral processing includes physical and chemical methods. The physical methods present, generally, minor environmental impacts; chemical methods, due to the use of different reagents (sodium carbonate, sodium hydroxide, sulphuric acid, etc.) present instead a greater environmental impact [5].

Lead and zinc most often occur in association with the sulphide mineral group, in particular, galena (PbS) and sphalerite (ZnS). Other metals, such as copper, iron, mercury, arsenic, cadmium, silver and small quantities of gold are associated with sulphide ores [5]. Natural weathering process entails the oxidation of metal sulphide minerals in the host rock and the formation of sulphuric acid could occur prior to mining. However, the consequent release of acid and metal mobilization poses a limited threat to the environment. Conversely, extraction and mineral processing associated with mining activity expose larger volumes of sulphide rock material to weathering processes increasing the metal mobilization [18]. Especially after the mine closure, the runoff and leaching from waste rock and tailings increase the oxidation of remaining sulphides, through chemical, electrochemical and biological

Table 1.1 Stages of mineral processing and main related impacts [4, 5]

Stages	Process	Impacts	Emission/waste
Extraction	Removal of ore material from a deposit and activities prior to beneficiation	Destruction of natural habitats and landscape Erosion caused by removal of vegetation Influence on hydrology around the excavated area Soil, water, and air pollution	Waste rock piles containing minerals associated with sulphide ores (chalcopyrite, pyrite, calcite, and dolomite) Wastewater from excavation phase Sediment run-off from mining sites. Acid mine drainage Wind dispersion of dust and greenhouse gas emissions
Beneficiation	Crushing, grinding, physical and chemical separation	Soil, water, and air pollution	Waste rock and tailings containing high concentration of metals and minerals, and toxic chemicals Wastewater containing dissolved solids and reagents Wind dispersion of dust and greenhouse gas emissions
Processing	Smelting and refining of concentrates	Air pollution	Emission of sulphur dioxide, arsenic, lead, cadmium, and other metals, dusts
Closure	Residues disposal	Contamination of surface, ground water, and air due to re-entrainment and/or subsequent deposition of particulates	Waste rock and tailings Acid mine drainage Leaching of pollutants from tailings Wind dispersion of dust from tailings

reactions; furthermore, it could generate ferric hydroxides and sulphuric acid combined in acidic mine drainage that increases the leaching potential of metals and their transport into ground water, surface water and soil [18–20].

This phenomenon is site specific depending on many factors: climate conditions, neutralization capacity of local materials, etc. [18, 19, 21, 22]. The effects on the environment can be mitigated by both prevention and treatment options: minimization of oxygen diffusion, control of pH of mineral wastes, solidification of wastes, inhibition of iron and sulphur oxidizing bacteria [23]. Although modern mines are equipped and managed with technologies suitable to prevent or attenuate their impacts, countries with a long mining history may present, in most cases, significant environmental impacts due to a poor management after mine closure [4, 24]. In fact, in modern mine, concentrations of As, Cd, Cu, Mn, Pb and Zn in tailings are as low as 1 g kg^{-1} while in historic mine they can be greater than 50 g kg^{-1} [10].

Numerous authors have evaluated the environmental contamination in the surrounding area of mining sites in different countries (among others, [25–33]). Recently, the spatial variability of Pb, Zn and Cd pollution in the mining sites of Bama mine (Iran) and surrounding urban areas has been evaluated by Dayani and Mohammadi [34]. Candeias et al. [20] assessed the levels of soil contamination in the Aljustrel mine (SW Portugal), with the aim to understand the partitioning and availability of pollutants in soil. The results showed a severe contamination (maximum concentration of Pb and Zn of 20000 mg kg^{-1}). Pb and Zn contamination due to former mining and smelting carried out in Plombières and La Calamine (Belgium) was evaluated by Cappuyns et al. [35].

The effect of mining and metallurgical activities in the neighbourhood of the Bolesław Mine and Metallurgical Plant in Bukowno (Poland) was evaluated by Agnieszka et al. [3] by germination inhibition and luminescence inhibition test for the assessment of ecological risks in soil and water. Impact of Pb and Zn mining activity on superficial sediments of Lake Kalimanci (FYR Macedonia) related to the weathering of tailings dam material was studied by Vrhovnik et al. [36].

The metals accumulation in soil determines direct and indirect effect on biotic communities. Metal accumulation in plants alters seed germination, plant growth, absorption and transport of essential elements. In addition, it can cause chlorosis, photosynthesis inhibition and mortality. A study done on wild rodents and plants, reported negative effects, such as loss of diversity of the biotic communities, due to metals bioaccumulation [37]. Moreover, soil contaminated from a Pb and Zn mine showed a decrease on both the biomass and diversity of the bacterial community in soil [38].

The metal fraction that, within a given time span, is either available or can be made available for uptake by plant in addition to the total metals concentration in soil, must be evaluated and also the metal chemical speciation must be identified in order to define the most suitable remediation technology [9, 39]. The speciation of trace metals depends on the physical and chemical characteristics of the soil: pH, redox potential, organic, carbonate, clay and oxide contents [9].

With the aim to predict the mobility and availability of metal in soil, different extraction methods have been developed [39, 40].

1.3 Phytoremediation Technologies Applied in Pb/Zn Mining Areas

Phytoremediation is a technology based on the capacity of plants to accumulate both metals which are essential elements for their growth (i.e. Zn) and metals which have no known biological function (i.e. Pb) [8, 41]. Technologies applicable for cleanup of Pb- and Zn-contaminated soils include phytoextraction (metals removal from soil and their concentration in the harvestable parts of plants) and phytostabilization (reduction of the mobility and bioavailability of metals in the environment) [41–43]. Plants suitable in phytoextraction should be tolerant to high metal concentration in soil, have the capability to accumulate great levels of metal in the harvestable part, have high growth rate and biomass production and finally have an extended root system [44].

In case of phytostabilization plants should be tolerant to the soil conditions, have high growth rate, provide a dense ground cover and have an extended root system. Moreover, plants must concentrate contaminant in a greater extent in root in comparison to aerial part [16]. Plant species that are capable of colonizing soils highly polluted by metals are defined metallophyte and pseudometallophyte species. Metallophytes, including hyperaccumulators, are endemic plant of natural mineralized soils which have developed physiological mechanisms of resistance and tolerance to the high metal concentration in soil and are generally characterized by a reduced production of biomass. Pseudometallophytes are native species common also in non-metalliferous soil which, due to selective pressure, are capable of surviving in soils highly polluted by metals [17].

Over 400 hyperaccumulator plants have been identified, some of these species, belonging to the Aceraceae, Brassicaceae, Caryophyllaceae, Cistaceae, Dichapetalaceae, Plumbaginaceae, Poaceae, Polygonaceae and Violaceae, in particular, were demonstrated capable of accumulating Pb and/or Zn [45–48]. Plants species are considered hyperaccumulators if metal concentration in shoots is >1000 and >10000 mg kg^{-1} of dry weight for Pb and Zn, respectively, when grown in metal-rich soils [49]. *Thlaspi caerulescens*, common in Western and Central Europe, can accumulate a maximum of 4 % of Zn in its dry matter and a less extent of Cd and Pb [46]. *Thlaspi rotundifolium* ssp. c*epaeifolium*, from a Pb and Zn mining area in Northern Italy has accumulated Pb at about 0.8 % of dry weight [45]. Recently, van der Ent et al. [50] has proposed a critical review on criteria commonly used to delimit hyperaccumulation of some metals and indicated lower limit. For instance, a limit lowered to 3000 mg kg^{-1} of dry weight was proposed for Zn. On the other side, excluders are plant species able to accumulate metals in roots limiting their transport into aerial parts, these plants are ideal candidate for phytostabilization process. Indicators accumulate metals in their aerial parts generally in proportion to the metal concentration in soil [51].

Previous investigations have demonstrated the accumulation potential of tree species, such as *Salix* spp., *Populus* L. and *Betula* L., when growing on metal-contaminated soils [43, 52–55]. Potential to accumulate metals in harvestable parts of *Salix* spp. (*Salix purpurea* L., *Salix caprea* L. and *Salix eleagnos* Scop.) collected from abandoned sulphide mine dumps has been evaluated [56]. The metal accumulation capacity evaluated by translocation factor (TF), ratio between metal concentration in shoots and metal concentration in roots, has shown significant differences among the species studied: *S. purpurea* was able to uptake and translocate Pb from roots to shoots (TF = 3.42) while *S. caprea* demonstrated similar ability for Zn (TF = 3.48), considering a soil with a mean Pb and Zn concentration of about 9600 and 1250 mg kg^{-1}, respectively. The metal translocation ability, combined with high biomass production makes these species suitable for phytoremediation and phytoextraction, in particular [56, 57].

Even agricultural and ornamental species have the capability to concentrate metals together with a high biomass production. *Brassica napus*, *Brassica juncea*, *Helianthus annuus* and *Zea mays* have been considered among others; generally, these species can be applied in a multi-metal-contaminated soil [58–60]. In case of use of agricultural species, some factors have to be taken into account: adaptability at the local climate conditions and soil agronomic properties, and tolerance to metal concentration in soil of the species chosen. The ornamental species *Mirabilis jalapa* L. has demonstrated its capacity to accumulate 1500 mg kg^{-1} of Pb in roots and about 400 mg kg^{-1} in the aerial part of the plant, from a soil with a Pb concentration of about 5500 mg kg^{-1} [61]. In case of phytoremediation of mining areas, native plants are preferable in comparison to introduced or invasive species, in order to reduce possible impact on the ecosystem [10, 62, 63]. Moreover, native plant species growing on mine tailings demonstrated a better tolerance to local conditions (climate, contamination and nutrient deficiency, etc.) [17, 64, 65]. Recently, different studies, summarized in Table 1.2, have been conducted in Pb and Zn mining areas in order to identify native plant species potentially relevant in phytoremediation.

In natural or continuous phytoremediation, plants with a $TF > 1$ are considered suitable species for phytoextraction, while species with a $TF < 1$ are generally considered suitable for phytostabilization and revegetation process. In addition, with the aim to modify accumulation characteristics of plants, soil amendments can be applied either to increase metal availability in soil (e.g. chelating agents or acidifying amendments), in case of assisted phytoextraction, or improve soil agronomic proprieties (e.g. fertilization), in case of aided phytostabilization [41, 66]. A field experiment was conducted by Zhuang et al. [67] with the aim to evaluate the effect of EDTA (ethylenediaminetetraacetic acid) in phytoextraction. Three plants were tested: *Viola baoshanensis*, *Vertiveria zizanioides* and *Rumex K-1 (Rumex patientia* × *R. Timschmicus*). Among the species tested, *V. baoshanensis* showed high potential for phytoremediation, and the application of EDTA enhanced Pb and Zn phytoextraction rates from 0.01 to 0.19 %, and 0.17 to 0.26 %, respectively. However, in assisted phytoextraction the chemical treatments can become a secondary cause of pollution. In fact, chelating agents, such as EDTA, are slowly biodegradable and increase the leachable metal fraction into ground water [68, 69]. In order to overcome these effects, biodegradable chelating agents should be applied [70].

In an assisted phytoextraction experiment in pots, Cao et al. [71] compared Pb and Zn phytoextraction by *M. jalapa*, using EDDS ([*S*,*S*]-ethylenediaminedisuccinic acid) and MGDA (methylglycinediacetic acid) in two different dosages (4 and 8 mmol kg^{-1} of soil). Both chelating agents demonstrated to increase Pb accumulation in leaves as well as improve bacterial activity in the soil. In the case of Zn, metal accumulation was independent from chelating agents application. However,

Table 1.2 Native plants species in phytoremediation experiment in mine soil contaminated by Pb and Zn (TF = translocation factor)

Plant species	Mine	Location	Metal concentration in soil (mean) [mg kg^{-1}]		TF		Reference
			Pb	Zn	Pb	Zn	
Achyrocline alata (Kunth) DC.	Hualgayoc	Peru	16060	28058	1.5	2.0	Bech et al. [103][a]
Ageratina sp.	Hualgayoc	Peru	16060	28058	0.4	0.6	Bech et al. [103][a]
Aster gymnocephalus A. Gray	Santa Maria	Mexico	4183	4546	2.0	20.5	Sánchez-López et al. [104]
Betula celtiberica	Rubiales	Spain	3000	20000	0.2	0.8	Becerra-Castro et al. [95]
Bidens triplinervia L.	Hualgayoc	Peru	13105	28393	0.13	0.16	Bech et al. [105]
Brickelia veronicifolia (Kunth) A. Gray	San Francisco	Mexico	1923	4745	0.6	1.4	Sánchez-López et al. [104]
Brickelia veronicifolia (Kunth) A. Gray	Santa Maria	Mexico	4183	4546	1.3	4.2	Sánchez-López et al. [104]
Cistus populifolius L.	Caveira	Portugal	4245	494	0.1	5.0	Abreu et al. [106]
Cistus populifolius L.	Chança	Portugal	141	66	0.11	2.53	Abreu et al. [106]
Cistus salviifolius L.	Campo Pisano	Italy	3260	12000	2.0	2.2	Cao et al. [107]
Cistus salviifolius L.	Chança	Portugal	141	66	0.2	2.93	Abreu et al. [106]
Cistus salviifolius L.	São Domingos	Portugal	4853	605	0.54	2.14	Abreu et al. [108]
Cistus salviifolius L.	Caveira	Portugal	7416	357	0.1	2.72	Abreu et al. [108]
Cistus salviifolius L.	Caveira	Portugal	4245	494	0.1	2.17	Abreu et al. [106]
Cistus salviifolius L.	São Domingos	Portugal	5901	294	0.34	2.59	Abreu et al. [106]
Cistus × hybridus	Caveira	Portugal	4245	494	0.11	5.32	Abreu et al. [106]
Cistus × hybridus	Chança	Portugal	141	66	1.5	2.74	Abreu et al. [106]
Cortaderia hapalotricha Pilg.	Hualgayoc	Peru	16060	28058	1.7	1.2	Bech et al. [103][a]

(continued)

Table 1.2 (continued)

Plant species	Mine	Location	Metal concentration in soil (mean) [mg kg^{-1}]		TF		Reference
			Pb	Zn	Pb	Zn	
Crotalaria pumila Ortega	Santa Maria	Mexico	4183	4546	1.1	11.6	Sánchez-López et al. [104]
Cuphea lanceolata Aiton	San Francisco	Mexico	1923	4745	0.6	6.7	Sánchez-López et al. [104]
Cytisus scoparius	Rubiales	Spain	3000	20000	0.2	0.4	Becerra-Castro et al. [95]
Dalea bicolor Humb. & Bonpl. Ex Willd.	San Francisco	Mexico	1923	4745	0.6	2.3	Sánchez-López et al. [104]
Dalea bicolor Humb. & Bonpl. Ex Willd.	Santa Maria	Mexico	4183	4546	0.9	3.3	Sánchez-López et al. [104]
Debregeasia orientalis	Beiya	China	2217	240	0.93	0.83	Liu et al. [109]
Dichondra argentea Willd.	San Francisco	Mexico	1923	4745	0.6	3.4	Sánchez-López et al. [104]
Dichondra argentea Willd.	Santa Maria	Mexico	4183	4546	0.8	1.3	Sánchez-López et al. [104]
Epilobium denticulatum Ruiz & Pav.	Hualgayoc	Peru	10128	23678	1.1	1.5	Bech et al. [103][a]
Festuca rubra	Rubiales	Spain	3000	20000	0.10	0.2	Becerra-Castro et al. [95]
Flaveria trinervia	Santa Maria	Mexico	4183	4546	1.0	10.9	Sánchez-López et al. [104]
Gnaphalium sp.	Santa Maria	Mexico	4183	4546	1.6	20.8	Sánchez-López et al. [104]
Hyparrhenia hirta	Cartagena-La Union	Spain	4200	15000	0.8	0.3	Conesa et al. [110]
Juniperus sp.	San Francisco	Mexico	1923	4745	1.1	17	Sánchez-López et al. [104]
Pteridium sp.	San Francisco	Mexico	1923	4745	0.2	0.2	Sánchez-López et al. [104]
Ruta graveolens L.	San Francisco	Mexico	1923	4745	1.0	2.5	Sánchez-López et al. [104]
Scrophularia canina subsp. bicolor	Campo Pisano	Italy	3260	12000	0.8	1.1	Cao et al. [107]
Senecio sp.	Hualgayoc	Peru	13105	28393	9.4	4.7	Bech et al. [105]
Taraxacum officinale Weber	Hualgayoc	Peru	14197	25829	0.6	0.4	Bech et al. [103][a]

(continued)

Table 1.2 (continued)

Plant species	Mine	Location	Metal concentration in soil (mean) [mg kg^{-1}]		TF		Reference
			Pb	Zn	Pb	Zn	
Tephrosia candida	Beiya	China	2207	256	0.85	0.77	Liu et al. [109]
Teucrium flavum L. subsp. *glaucum*	Campo Pisano	Italy	3260	12000	1.6	0.7	Cao et al. [107]
Trifolium repens Walter	Hualgayoc	Peru	10128	23678	1.5	1.3	Bech et al. [103][a]
Viguiera dentata (Cav.) Spreng.	San Francisco	Mexico	1923	4745	0.5	0.9	Sánchez-López et al. [104]
Viguiera dentata (Cav.) Spreng.	Santa Maria	Mexico	4183	4546	0.6	2.0	Sánchez-López et al. [104]
Zygophyllum fabago	Cartagena-La Union	Spain	4800	13000	0.7	1.5	Conesa et al. [110]

[a]Data referring to the substrate having the higher metal concentrations

both EDDS and MGDA demonstrated to be toxic to the plant causing death at maximum dose. Response of treatment with chelating agents seems to be related to the dosages applied [72–75].

The application of complementary techniques such as additives application and fertilization could improve phytostabilization results [76, 77]. The organic amendments, as compost, increase the content of essential nutrients of soil (C, N, P, K), which improve plant growth and stimulate the microbial activities. The effectiveness of these treatments for the reduction of soil risks have been confirmed by ecotoxicological tests with bacteria *Vibrio fischeri,* crustaceans *Daphnia magna* and *Thamnocephalus platyurus* and earthworm *Eisenia fetida* tests [78, 79].

A greenhouse experiment was conducted by Lee et al. [80] to evaluate the effect of four different amendments (bone mill, bottom ash, furnace slag and red mud) as immobilizing agents and two Korean native plant species, *Miscanthus sinensis* and *Pteridium aquilinum,* in aided phytostabilization of Pb and Zn mine tailings. Results of the study suggest that *M. sinensis* is appropriate for phytostabilization, since it accumulated heavy metals mainly in the root, and had lower translocation factors compared with *P. aquilinum;* furthermore, amendments such as furnace slag and red mud are effective at reducing the availability and mobility of metals. Recently, phytostabilization experiments have been carried out in field with the use of native species, selected on the basis of their ability to survive and regenerate in the local environment.

The area of the experiments performed by de la Fuente et al. [81], was located downstream the Aznalcóllar mine (Spain) [82], previously object of different phytoremediation experiments [83]. Native species (*Retama sphaerocarpa, Tamarix gallica, Rosmarinus officinalis* and *Myrtus communis*) were grown under natural conditions, without any agricultural practice or irrigation system, in soil with a maximum metal concentration of about 839 and 1617 mg kg^{-1} for Pb and Zn, respectively. The results permitted to identify the *R. sphaerocarpa* as the most adequate plant species for soil restoration. At the end of the experiment, *R. sphaerocarpa* showed the highest percentage of plant survival (44 %), the ability to grow in soils with poor agronomic properties and acidic conditions, and the lower bioconcentration factor (i.e. metal concentration in shoot tissues versus total metal concentration in soil) equal to 0 and 0.19 for Pb and Zn, respectively.

Results from an application of P fertilizers (phosphate rock, calcium magnesium phosphate and single superphosphate) in field plots planted with *Brassica chinensis* L. *campestris* indicate that these amendments induced immobilization of metals such as Pb, Cd and Zn [84].

The phytostabilization experiment performed in the tailings dam of Campo Pisano (Sardinia, Italy), consisted in the use of different soil amendments, compost, chemical fertilizer and zeolites, used singly or in combination. In general, all amendments reduced the bioavailable metal fraction; in particular, compost proved to be the best amendment in the long-term for plant growth. Among the plant species tested (*Scrophularia canina* subsp. *bicolor Greuter* and *Pistacia lentiscus*) *P. lentiscus* appears to be the most suitable species for phytostabilization and revegetation, both for its resistance to metals and high phytomass production [85].

Galende et al. [86] evaluated the application of combined organic amendments (cow slurry, poultry manure and paper mill sludge mixed with poultry manure) in a phytostabilization experiment on an abandoned Pb and Zn mine located in the province of Biscay (Basque Country, Spain) with *Festuca rubra L.* species. Amendment application demonstrated to promote biomass production in *F. rubra* and caused a reduction in bioavailable Pb and Zn in soils. Further investigations focusing on phytoremediation of Pb and Zn mine areas have been conducted also by applying non-native species as reported in Table 1.3.

An additional aspect to be considered is that plants play an important role in reducing dispersion of soil-contaminated particles from mine tailings caused by atmospheric agents. Recently, the role of leaves of plants growing spontaneously on mine tailings acting as a barrier for the dispersion of particles containing potentially toxic elements has been evaluated [87]. Comprehensive reviews, summarizing the most important aspects of phytoremediation processes and physiological mechanisms of metal accumulation in plants are available (Table 1.4).

Table 1.3 Assisted phytoremediation experiments in mine soils contaminated by Pb and Zn

Plant species	Location	Pb in soil Total (mg kg^{-1})	Zn in soil Total (mg kg^{-1})	Pb in soil Extractable (mg kg^{-1})	Zn in soil Extractable (mg kg^{-1})	Details on extraction agent	Amendments	Reference
Triticum aestivum L.	Příbram (Czech Republic)	3035	4900	266	2925	Acetic acid	Digestate (biowaste anaerobic fermentation)	García-Sánchez et al. [111]
							Fly ash (wood chip combustion)	
							$(NH_4)_2SO_4$	
Mirabilis jalapa L.	Montevecchio-Ingurtosu (Italy)	5357	1767	3426	432	EDTA	Clinoptilolite	Lai et al. [61]
							Clinoptilolite NH_4^+-charged	
							Clinoptilolite CO_2-charged	
Zygophyllum fabago L.	Cartagena-La Unión (Spain)	–	–	277	495	DTPA	Pig manure + marble waste	Zornoza et al. [112]
Piptatherum miliaceum (L.) Coss.							Sewage sludge + marble waste	
Dittrichia viscosa (L.) Greuter								
Phragmites australis (Cav.) Trin. ex Steud								
Helichrysum decumbens DC.								
Sonchus tenerrimus L.								

(continued)

Table 1.3 (continued)

Plant species	Location	Pb in soil Total (mg kg^{-1})	Zn in soil Total (mg kg^{-1})	Pb in soil Extractable (mg kg^{-1})	Zn in soil Extractable (mg kg^{-1})	Details on extraction agent	Amendments	Reference
Vertiveria zizanioides	Lechang (China)	960	1050	119	93	DTPA	EDTA (ethylenediaminetetracetic acid)	Zhuang et al. [113]
Dianthus chinensis								
Rumex K-1 (Rumex upatientia × R. timschmicus)								
Rumex crispus								
Viola baoshanensis								
Sedum alfredii								
Brachiaria decumbens	Biscay (Spain)	4166	15277	–	–	–	EDTA (ethylenediaminetetracetic acid)	Santos et al. [114]
							EDDS (ethylenediaminedisuccinate)	
Vetiveria zizanioides	Lechang (China)	1155	1583	361	834	DTPA	Manure compost	Chiu et al. [115]
Phragmities australis							Sewage sludge	
Helianthus annuus	Bama (Iran)	1564	2739	29	182	DTPA	DTPA (diethylenetriaminepentaacetic acid)	Solhi et al. [116]
Brassica napus							Composted manure	
							Sulphuric acid	

Viola baoshanensis	Lechang (China)	2078	2472	177	161	DTPA	EDTA (ethylenediaminetetracetic acid)	Zhuang et al. [67]
Vertiveria zizanioides							$(NH_4)_2SO_4$	
Rumex K-1 (Rumex patientia · R. timschmicus)							NH_4NO_3	
Vetiveria zizanioides	Lechang (China)	4164	4377	331	187	DTPA	Domestic refuse	Yang et. [117]
Sesbania rostrata							Inorganic fertilizer	
Sesbania sesban								

Table 1.4 Selection of reviews related to phytoremediation of metals

Content	References < 2005	References > 2005
Source of contamination and its effects on the environment and human health	McLaughlin et al. [8]	Wuana and Okieimen [2]
		Bolan et al. [12]
		Su et al. [118]
Mining area specificity related to reclamation	Bradshaw [13]	Mendez and Maier [10]
	Tordoff et al. [14]	Li [119]
	Singh et al. [15]	
Availability of contaminants	Peijnenburg and Jager [39]	Leštan et al. [75]
	Kabata-Pendias [40]	Ali et al. [69]
		Bolan et al. [12]
Remediation technologies, including physical, chemical, and biological remediation	Mulligan et al. [9]	Marques et al. [16]
		Wuana and Okieimen [2]
		Yao et al. [11]
		Su et al. [118]
Phytoremediation techniques applicable in metal-contaminated soil including continuous and assisted phytoremediation	Salt et al. [41]	Li [119]
	Raskin et al. [58]	Evangelou et al. [73]
	Garbisu and Alkorta [44]	Padmavathiamma and Li [120]
	Singh et al. [15]	Mendez and Maier [10]
	McGrath and Zhao [121]	Marques et al. [16]
	Alkorta et al. [122]	Robinson et al. [51]
	Arthur et al. [123]	Vangronsveld et al. [66]
		Wu et al. [124]
		Vamerali et al. [60]
		Wuana and Okieimen [2]
		Cameselle et al. [125]
		Bolan et al. [12]
		Favas et al. [17]
		Gupta et al. [126]

Plants species suitable for remediation with particular focus on metallophytes (hyperaccumulators, excluders, indicators)	Singh et al. [15]	Padmavathiamma and Li [120]
	McGrath and Zhao [121]	Marques et al. [16]
	Yang et al. [127]	Robinson et al. [51]
		Sheoran et al. [128]
		Kavamura and Esposito [129]
		Rascio and Navari-Izzo [47]
		Bhargava et al. [130]
		van der Ent et al. [50]
		Ali et al. [69]
		Visioli and Marmiroli [131]
		Pollard et al. [48]
		Ullah et al. [132]
Plants species suitable for remediation (crops species, tree species, …)	Pulford and Watson [43]	Vamerali et al. [60]
		Bhargava et al. [130]
Parameters for evaluation of process efficiency	USEPA [133]	Robinson et al. [51]
		Wuana and Okieimen [2]
		Ali et al. [69]
		Favas et al. [17]
Genetic engineering plants	Garbisu and Alkorta [44]	Kotrba et al. [101]
	Pilon-Smits and Pilon [99]	Marques et al. [16]
	McGrath and Zhao [121]	Vangronsveld et al. [66]
	Eapen and D'Souza [134]	Wu et al. [124]
	Yang et al. [127]	Vamerali et al. [60]
		Bhargava et al. [130]

(continued)

Table 1.4 (continued)

Rhizosphere microbial community and its role in phytoremediation	Garbisu and Alkorta [44]	Lebeau et al. [135]
	Glick [136]	Marques et al. [16]
		Kavamura and Esposito [129]
		Glick [137]
		Vamerali et al. [60]
		Ma et al. [90]
		Bhargava et al. [130]
		Rajkumar et al. [138]
		Rajkumar et al. [139]
		Ullah et al. [132]
Economic aspects and costs evaluation	Glass [140]	Robinson et al. [51]
		Vangronsveld et al. [66]
		Wuana and Okieimen [2]

1.4 Synergistic Effects of Plants and Bacteria in Phytoremediation

Interactions between plant and rhizosphere microbial communities in Pb and Zn mine soil have been evaluated [88, 89]. Bacterial populations associated with plants growing in metalliferous soils should improve plant growth and nutrition by nitrogen fixation, production of phytohormones and siderophores, transformation of nutrient elements and by increasing metal tolerance and accumulation due to the capacity of microorganisms to increase bioavailable metals fraction, through the release of chelating agents, acidification, phosphate solubilization and redox changes [90–93].

The administration of selected plant growth-promoting bacteria can significantly speed up the phytostabilization process by improving plant establishment, growth and health as demonstrated in a bioaugmentation-assisted phytostabilization process based on autochthonous plant species and bacterial inocula from abandoned Sardinian mining areas (Italy) [94]. In a recent study, the plant-microorganism-soil system of three pseudometallophytes identified as metal excluders (*Betula celtiberica*, *Cytisus scoparius* and *Festuca rubra*) growing in a Pb and Zn mine was characterized. Becerra-Castro et al. [95] isolated metal-tolerant rhizobacteria from rhizosphere of selected plant species and verified, in a pot experiment, the effect of a re-inoculum of the rhizobacteria on growth and metal uptake of *Festuca pratensis* Huds. and *Salix viminalis* L., commonly used in phytoremediation. As a result, authors demonstrated that some of the plant-associated bacteria isolated from mine site could be exploited for improving plant growth, and performance, in metal-contaminated soil.

The effects of chelating agent's application in phytoextraction experiment have been, also, investigated. In an assisted phytoextraction process with *Cynara cardunculus*, the treatment with a single dose (1 g kg^{-1} of soil) of two chelating agents (EDTA and EDDS) on soil microorganisms has been evaluated through the determination of biological indicators of soil quality (i.e. enzyme activities, basal and substrate-induced respiration) [74]. EDTA was more efficient than EDDS in enhance root Pb uptake and root-to-shoot Pb translocation. However, EDDS was more rapidly degraded, and less toxic to the soil microbial community in control non-polluted soils. Pb-polluted soils treated with EDDS showed significantly higher values of basal and substrate-induced respiration than those treated with EDTA. In pots experiment with *Mirabilis jalapa*, the application of easily biodegradable chelating agents (EDDS and MGDA) seemed to have a positive influence on bacterial communities both in bulk soil and in the rhizosphere, whereas the endophytes were less affected by the treatments [71].

1.5 Genetically Engineered Plants for Phytoremediation

The genetically engineered plants (GEPs) have been considered in the last decades with the aim to evaluate their potential use in phytoremediation [96, 97]. In this frame, the goal of genetic engineering is to modify characteristics of plant species, such as metal uptake, transport and accumulation, and metal tolerance to enhance remediation efficiency (see related references in Table 1.4). Among different plant species growing on highly contaminated soils by metals in Eastern Spain, *Nicotiana glauca* R. Graham was selected for subsequent gene transfer (gene transferred: wheat gene-encoding phytochelatin synthase TaPCS1) because of its resistance to metals and physiological characteristics appropriate for phytoremediation [98]. Results demonstrated the increase of *N. glauca* tolerance to metals, such as Pb and Cd, and a higher accumulation Pb capacity in comparison of wild species in pot experiment with a Pb- and Zn-contaminated soil from a mine area.

When GEPs are used for applications in phytoremediation, the potential environmental risk needs to be considered. Possible risks include biological transformation of metals in more bioavailable forms, higher exposure of wildlife to metals in case of accumulation in palatable part of the plants, uncontrolled diffusion of transgenic plants [99–101]. Related to the latter, in order to control undesirable genetic spreading, Shim et al. [102] tested the non-flowering mutant poplar clone *Populus alba* × *P. tremula var. glandulosa,* transforming the plants with a metal resistance gene, ScYCF1 (yeast cadmium factor 1), and tested these transgenic plants in soil taken from a closed mine site contaminated with multiple toxic metals (As = 2171 mg kg^{-1}, Pb = 447 mg kg^{-1}, Zn = 2343 mg kg^{-1}) under greenhouse and field conditions. The results demonstrate that YCF1-expressing poplar plants have a higher tolerance to contaminated mining soil and higher metal accumulation capacity than control and are suitable for phytostabilization process of mine areas.

1.6 Conclusions

Phytoremediation is generally recognized as a cost-effective and environmental sustainable technology compared to physical and chemical remediation technologies. An extensive literature exists on the application of phytoremediation to soil contaminated by mining activity. Lead and zinc, extracted from sulphide ores, are among the most common contaminants in soils originated by mineral exploitation; both phytoextraction and phytostabilization can be applied in this case. However, it is well acknowledged that each mine site possesses specific physicochemical characteristics, and thus the identification of the ideal candidate for phytoremediation must be tailored on the individual mine site. Recently, greater attention is addressed to apply native plant species, which demonstrated a better tolerance to local conditions, and are preferable in comparison to introduced or invasive species in order to reduce possible impact on the ecosystem. On the basis of experimental results, phytoextraction of heavily polluted soils may be required decades to reduce the residual metal concentration to acceptable levels. In order to overcome this issue, assisted phytoextraction has been introduced, based on the use of chelating agents or acidifying amendments, aiming at lowering reclamation times and increasing process efficiency. However, the application of chemical treatments can become a secondary cause of pollution.

Taking into account the characteristics of mine areas, in particular size and level of contamination, phytostabilization seems the most preferable technique, while phytoextraction could be applied in areas surrounding mine sites when soil contamination is limited. Again, the use of amendments such as compost or fertilizers could enhance the process by improving the soil properties and assisting the plant growth. Finally, different studies are being conducted to evaluate potential use of genetically engineered plants for phytoremediation, but the environmental benefits and risks associated with GEPs should be carefully evaluated before field applications.

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