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Metal Mine Waste and Phytoremediation: A Review

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Abstract: Phytoremediation is a group of technologies that use plants to reduce, remove, degrade, or immobilize environmental toxins, primarily those of anthropogenic origin, with the aim of restoring area sites to a condition useable for private or public applications. The poor physical structures, acidity, lack of nutrients, presence of toxic heavy metals are the common characteristics of mine tailings. Bare tailings are prone to erosion, resulting in further environmental degradation as the very young soils develop on unstable materials with low cohesion. Appropriate vegetative cover of such bare tailings can overcome the adverse physical and chemical properties of them. Collecting naturally growing plant species on such tailings and the evaluation of plant metal concentrations can be used to get information about specific plant behaviour in this environment. Thus considering the diversity of plant responses in contaminated sites having different metal and toxicity levels, at various levels, it is important to study the composition of plant community that was established on metal enriched tailings that would serve as a basic approach for phytoremediation. In this paper, general aspects of phytoremediation processes, plant response to soil heavy metals, the pathway of metal in plants, different extraction methods used for prediction of plant availability of metals in soil and outcome of various studies regarding trace metal contents and their accumulation in plant species growing on metal enriched spoils/tailings are reviewed.

Key words: Phytoremediation, heavy metals, metal accumulation in plants.

Introduction

The global budget of toxic trace elements has increased dramatically due to a variety of activities since the dawn of industrial revolution. Mining activities such as crushing, grinding, washing, smelting and all the other processes used to extract, concentrate metals generate a large amount of waste rocks, and tailings are often very unstable and make toxic elements environmentally labile through normal biogeochemical pathways, to sink such as sediments, soils or biomass. The direct effect will be loss of cultivated land, forest or grazing land, and the overall loss of production (Wang, 2003). The indirect effects include air and water pollution and siltation of water body. This will eventually lead to the loss of biodiversity, amenity, and economic wealth (Breadshaw, 1993). Establishment of vegetation cover can fulfil the objectives of stabilisation, pollution control, visual improvement, and removal of threats to human beings (Freitas et al., 2004). However, adverse factors such as acidity, nutrient deficiencies, toxic heavy metal ions, and poor physical structure, and their interaction of most mine tailings inhibit plant establishment and growth on the tailings (Pichtel and Salt, 1998).

Mine spoil or tailing dumps usually have barren surfaces, with rare plants that show signs of suffering such as stunted growth, chlorosis, nacrosis and anomalous development of roots with respect to shoots (Dinelli and Lombini, 1996). Collecting plant species on contaminated soil and the evaluation of plant metal concentrations can be used to get information about specific plant behaviour in this environment and to complete data about metal dispersion, with reference to their mobility to the biomass. Metal concentration in plants is a function not only of the total soil concentrations but depend also on the chemical speciation of metals in soil solutions (Kabata-Pendias and Pendias, 1992) and on the involvement of the metal in biological functions (Adriano, 1986). Some plants phytostabilise heavy metals in the rhizosphere through root exudates immobilisation (Blaylock and Huang, 2000) whilst other species incorporate them into root tissues (Khan, 2001). Some plant also transfers metals to their aboveground tissues, potentially allowing the soil to be decontaminated by harvesting the aboveground parts. Therefore, plant community established on mine spoil/tailings could be useful to minimize the impacts of mining. Thus considering the diversity of plant responses in contaminated sites having different metals and toxicity levels, at various levels, it is important to study the composition of plant community that was established on degraded soils or mine spoil, which would serve as a basic approach for mine remediation.

Phytoremediation Processes

Phytoremediation is a term applied to a group of technologies that use plants to reduce, remove, degrade, or immobilize environmental toxins, primarily those of anthropogenic origin, with the aim of restoring area sites to a condition useable for private or public applications. To date, phytoremediation efforts have focussed on the use of plants to accelerate degradation of organic contaminants, usually in concert with root rhizosphere microorganisms, or remove hazardous heavy metals from soils or water. Phytoremediation of contaminated sites is appealing because it is relatively inexpensive and aesthetically pleasing to the public compared to alternate remediation strategies involving excavation/removal or chemical in situ stabilization or conversion. Phytoremediation processes include:

Phytoextraction: It involves the removal of toxins, especially heavy metals and metalloids, by the roots of the plants with subsequent transport to aerial plant organs (Salt et al., 1998). Pollutants accumulated in stems and leaves are harvested with accumulating plants and removed from the site. It can be divided into two categories: continuous and induced (Salt et al., 1998). Continuous phytoextraction requires the use of plants that accumulate particularly high levels of the toxic contaminants throughout their lifetime (hyperaccumulators), while induced phytoextraction approaches enhance toxin accumulation at a single time point by addition of accelerants or chelators to the soil. However, there may be risks associated with using certain chelators considering the high water solubility of some chelators-toxin complexes, which could result in movement of the complexes to deeper soil layers (Lombi et al., 2001) and potential ground water and estuarine contamination.

Phytodegradation: In phytodegradation, organic pollutants are converted by internal or secreted enzymes into compounds with reduced toxicity (Salt et al., 1998). For instance, the major water and soil contaminant trichloroethylene (TCE) was found to be taken up by hybrid poplar trees, *Populus deltoides nigra,* which breaks down the contaminant into its metabolic components (Newman et al., 1997).

Phytovolatization: Plants can also remove toxic substances, such as organics, from the soil through phytovolatization. In this process, the soluble contaminants are taken up with water by the roots, transported to the leaves, and volatilized into the atmosphere through the stomata (Newman et al., 1997). Selenium (Se) is a special case of a metal that is taken up by plants and volatilized. Se can also be volatilized following conversion to dimethylselenide by microbes and algae (Neumann et al., 2003).

Rhizosphere degradation: Like phytodegradation, rhizosphere degradation involves the enzymatic breakdown of organic pollutants, but through microbial enzymatic activity. These breakdown products are either volatilized or incorporated into the microorganisms and soil matrix of the rhizosphere. The types of plants growing in the contaminated area influence the amount, diversity, and activity of microbial populations (Kirk et al., 2005). Grasses with high root density, legumes and alfalfa that fix nitrogen and have high evapotranspiration rates are associated with different microbial populations. These plants create a more aerobic environment in the soil that stimulates microbial activity that enhances oxidation of organic chemical residues (Kirk et al., 2005).

Rhizofiltration: It removes contaminants from water and aqueous waste streams, such as agricultural run off, industrial discharges, and nuclear material processing wastes (Salt et al., 1998). Absorption and adsorption by plant roots play key role in this technique, and consequently large root surface areas are usually required.

Phytostabilization: Erosion and leaching can mobilize soil contaminants resulting in aerial or water-borne pollution of additional sites. In phytostabilization, accumulation by plant roots or precipitation in the soil by root exudates immobilizes and reduces the availability of soil contaminants. Plants growing on polluted sites also stabilize the soil and can serve as a groundcover thereby reducing wind and water erosion and direct contact of the contaminants with animals. Plants with high transpiration rates, such as grasses, sedges, forage plants, and reeds are useful for phytostabilization by decreasing the amount of ground water migrating away from the site carrying contaminants. Combining these plants with hardy, perennial, dense rooted or deep rooting trees (poplar, cottonwoods) can be an effective combination (Berti and Cuningham, 2000).

Phytorestoration: It involves the complete remediation of contaminated soils to fully functioning soils (Bradshaw, 1997). In particular, this subdivision of phytoremediation uses plants that are native to the particular area, in an attempt to return the land to its natural state.

Hydraulic Influence: In this process, trees aid remediation by influencing groundwater movement. Trees act as natural pumps when their roots reach downwards to the water table and establish a dense root mass that takes up large quantities of water (e.g., mature cottonwoods can absorb 350 gallons per day).

Plant Response to Heavy Metals

When categorizing plants that can grow in the presence of toxic elements, the terms "metal excluder", "metal indicator", and "metal accumulator" are used. Metal excluders prevent metal from entering their aerial parts or maintain low and constant metal concentration over a broad range of metal concentration in soil; they mainly restrict metal in their roots. The plant may alter its membrane permeability, change metal binding capacity of cell walls, or exclude more chelating substances (Lasat, 2000).

A metal indicator species is one that actively accumulates metal in their aerial tissues and generally reflects metal level in soil. They tolerate the existing concentration level of metals by producing intracellular metal binding compounds (chelators), or alter metal compartmentalization pattern by storing metals in non-sensitive parts (Ghosh and Singh, 2005).

Metal accumulators can concentrate metal in their aerial parts, to levels far exceeding than soil. Hyperaccumulators are plants that can absorb high levels of contaminants concentrated in roots, shoots, and/or leaves. The metal/metalloid concentration that must be accumulated by the plant before it is designated a "hyperaccumulator" depends upon the particular metal or metalloid in question. In early hyperaccumulator studies, Baker and Brooks (1989) have defined metal hyperaccumulator as plants that contain more than or upto 0.1% (1000 mg kg^{-1}) of Ni, Cu, Co, Pb or 1% of Zn or Mn in the dry matter. For cadmium and other rare metals, it is 0.01% by dry weight. Hyperaccumulators are found in 45 different families, with the highest occurrence among the *Brassicaceae* (Reeves and Baker, 2000). These plants are quite varied, from perennial shrubs and trees to small annual herbs.

How Do Plants Take up and Transport Metal?

The process of metal accumulation involves several steps, one or more of which are responsible for the hyperaccumulation in plants:

Solubilization of the metal from the soil matrix: Many metals are found in soil-insoluble forms. Plants use two methods to desorb metals from the soil matrix: acidification of the rhizosphere through the action of plasma membrane proton pumps and secretion of ligands capable of chelating the metal. Plants have evolved these processes to liberate essential metals from the soil, but soils with high concentrations of toxic metals will release both essential and toxic metals to solution (Lasat, 2000).

Uptake into the root: Soluble metals can enter into the root symplast by crossing the plasma membrane of the root endodermal cells or they can enter the root apoplast through the space between cells. While it is possible for solutes to travel up through the plant by apoplastic flow, the more efficient method of moving up the plant is through the vasculature of the plant, called the xylem. To enter the xylem, solutes must cross the Casparian strip, a waxy coating, which is impermeable to solutes, unless they pass through the cells of the endodermis. Therefore, to enter the xylem, metals must cross a membrane, probably through the action of a membrane pump or channel. Most toxic metals are thought to cross these membranes through pumps and channels intended to transport essential elements. Excluder plants survive by enhancing specificity for the essential element or pumping the toxic metal back out of the plant (Hall, 2002).

Transport to the leaves: Once loaded into the xylem, the flow of the xylem sap will transport the metal to the leaves, where it must be loaded into the cells of the leaf, again crossing a membrane. The cell types where the metals are deposited vary between hyperaccumulator species.

Detoxification and/or Chelation: At any point along the pathway, the metal could be converted to a less toxic form through chemical conversion or by complexation. Various oxidation states of toxic elements have very different uptake, transport, and sequestration or toxicity characteristics in plants. Chelation of toxins by endogenous plant compounds can have similar effects on all of these properties as well. As many chelators use thiol groups as ligands, the sulfur (S) biosynthetic pathways have been shown to be critical for hyperaccumulator function (Van Huysen et al., 2004) and for possible phytoremediation strategies.

Sequestration and volatilization: The final step for the accumulation of most metals is the sequestration of the metal away from any cellular processes it might disrupt. Sequestration usually occurs in the plant vacuole, where the metal/metal-ligand must be transported across the vacuolar membrane. Metals may also remain in the cell wall instead of crossing the plasma membrane into the cell, as the negative charge sites on the cell walls may interact with polyvalent cations (Wang and Evangelou, 1994). Selenium may also be volatilized through the stomata.

Total and Bio-available Fraction of Heavy Metals in Soil

Heavy metals are elements having atomic weight between 63.54 and 200.9 and a specific gravity greater than 4.0 (Kennish, 1992). Trace amount of some heavy metals are required by living organisms; however any excess amount of these metals can be detrimental to the living organisms. Nonessential heavy metals include arsenic, antimony, cadmium, chromium, mercury, lead etc.; these metals are of particular concern to surface water and soil pollution (Kennish, 1992). Heavy metals exist in colloidal, ionic, particulate, and dissolved phase. Metals also have a high affinity for humic acids, organo clays, and oxides coated with organic matter. The soluble forms are generally ions or unionized organometallic chelates or complexes. The pH, amount of metal, cation exchange capacity, organic carbon content, the oxidation state of the mineral components, and the redox potential of the system predominantly control the solubility of metals in soil and ground water. In general, soil pH seems to have the greatest effect of any single factor on the solubility or retention of metals in soils, with a greater retention and lower solubility of metal cations occurring at high soil pH. Under the neutral to basic conditions typical of most soils, cationic metals are strongly adsorbed on the clay fractions and can be adsorbed by hydrous oxides of iron, aluminium, or manganese present in soil minerals. Elevated salt concentration creates increased competition between cations and metals for binding sites. In addition, competitive adsorption between various metals has been observed in experiments involving various solids with oxide surfaces. In several experiments, Cd adsorption was decreased by the addition of Pb or Cu (Ghosh and Singh, 2005).

Status of Heavy Metals in Mine Spoil/Tailings

Total DTPA-extractable and total dissolved contents of Cd, Cr, Cu, Ni, Pb and Zn were determined in minesoils of two mining areas, Touro Copper mine and Meirama lignite mines located in Galicia, Spain. The total dissolved heavy metal (< 2 mg/kg) and DTPA-extractable contents were low in all the soils except the Cu-dissolved content in soils from Cu mine spoils. The Cu, Cr and Zn total content in Cu mine soil was reported higher than lignite mine soil but DTPA-extractable Zn and Cr were found higher in the latter. The proportion of DTPA-extractable Cd in lignite minesoil was 11.48% although the total content was low (< 5 mg/kg) and in Cu minesoil it was absent. Dissolved Cd was not found in any minesoils. The relation established between the soil organic matter content and the humified organic matter, with the total DTPA-extractable Cu content, indicates that the humified organic matter was the fraction involved in the formation of soluble complexes and in the electrostatic adsorption of Cu. This demonstrates the capacity of the organic matter to establish not only soluble complexes but also insoluble compounds with Cu. A positive correlation was also found between the DTPA-extractable Cu, Fe and Mn oxides content, which probably indicates that the Cu^{2+} can be partly adsorbed by oxides. The origin of the Zn, Ni and Cr contents of minesoils was confirmed by means of the established positive correlation between the total content of these metals which indicates that these metals came from the minerals of the parent matter of Cu minesoils (chalcopyrite, amphibolites and limonite) (Vega et al., 2004).

The concentrations of different forms of heavy metals (Fe, Cu, Mn, Zn, Ni, Co and Pd) were determined in an iron-ore-tailing and compared with those of the natural vegetation colonizing on the dump. Tailings had neutral pH (6.14) and low electrical conductivity (55.9 mS/cm). Four forms of metals, total, bioavailable, acid extractable and water-soluble were studied. Iron was the most abundant metal in all forms and the relative abundance of metals were as follows: Fe> Mn> Zn> Cu> Ni> Pb> Co. The average concentration of total Fe was 41,670 mg/kg, total Mn 86 mg/kg, total Cu 23 mg/kg, total Zn 30 mg/kg and Pb, Ni, Co were found in traces. The fraction of bioavailable to total metal for Fe was (0.03%), Mn (6.0%), Zn (3.8%) and Cu (1.8%). The concentrations of acid extractable fractions were as follows: Fe 215 $mgkg^{-1}$, Mn 25 mg/kg, Zn 2.40 mg/kg, Cu 1.68 mg/kg, Ni 1.10 mg/kg, Pb 0.62 mg/kg and Co in traces. In water extract solution, only Fe (0.4 mg/kg) was present (Maiti and Nandini, 2005)

High levels of As, Cu, Pb and Zn were reported in the degraded soil of Sao Domingos mine in the southeast Portugal. Copper concentration in soils could reach 1829 mg/kg as a result of the former smelting activities. Maximum concentration of As in soils was very high, reaching 1291 mg/kg. The concentration of Pb in soil was also very high, 2693.7 mg/kg as the average value registered. The average Zn concentration in soil was of 218.2 mg/kg but it could reach 713.7 mg/kg, a level that can be extremely toxic for plants. Co and Cr concentrations in soils were normally low, ranging from 20.1-54.3 mg/kg and 5.1-84.6 mg/kg for Co and Cr respectively. Ni and Ag were also low, varying from 27.2-52.9 for Ni and 2.5-16.6 mg/kg for Ag (Freitas et al., 2004).

A study was carried out to investigate the total and the phytoavailability of trace elements to vegetables grown on metal contaminated calcareous soil in northern China. Amount of total trace elements in soils varied widely (Cr 9.0-160, Ni 6.4-46.4, Zn 7.9-205, Cu 6.7-234, Cd 0.0538-4.08, Pb 20.2-210, La 1.8-49.6, Ce 3.15-107, Pr 0.391-15.2 and Nd 1.54-45.4 ng/g) among sample sites. Four frequently used methods using $CaCl_2$, DTPA, CH_3COOH, and water as extractant was compared for phytoavailability. The concentrations of metals extracted by these four extraction methods ranged from 3.42-815, 1.51-6965, 0.732-24473, 0.688-7863, 0.246-685, 1.99-5337 ng/g for Cr, Ni, Zn, Cu, Cd, Pb and REEs respectively (Wang et al., 2004).

Lechang Pb/Zn mine (Nothern Guangdong, China) contained high levels of total and DTPA extractable Pb (4164 and 331 mg/kg) and Zn (4377 and 187 mg/kg), and low levels of micronutrients (N, P, K) and organic materials. The total and extractable concentrations of Pb and Zn greatly exceeded the background values of normal soil (Pb 22.5, Zn 29.0 mg/kg) and nutrient contents and organic matter were much lower than normal soil (Yang et al., 2003).

San Finx mine is located in western Galicia (NW Spain) and mining activity ceased in 1989. The concentrations of different forms of heavy metals (total, bioavailable, exchangeable and soluble) were determined in this mine dump material, rich in chalcopyrite. The most abundant heavy metal, both in total and bioavailable forms was iron, followed by Cu, Mn, Zn and chromium. Concentration of Cd and Pb were below detection limits. Cu was the most abundant metal in the aqueous extracts and on the cation exchange sites, followed by Zn, Mn and iron. A high proportion of bioavailable Cu and Zn was in exchangeable form; in contrast, a minor fraction of bioavailable iron was exchangeable. The variance of the concentrations of bioavailable, exchangeable and soluble Cu and Zn depended mainly on the cation exchange capacity of the soil. The total contents of Cu (274-5421 mg/kg) and in some instances Mn (295-2105 mg/kg) and Zn (74-895 mg/kg), exceeded the limits of phytotoxicity (100, 1500 and 300 mg/kg for Cu, Mn and Zn respectively) as reported by Kabata-Pendias and Pendias (1992). The bioavailable forms constituted between 0.5 and 20% of total Fe, between 1 and 85% of total Cu, between 0.3 and 6% of total Mn and between 0.7 and 38% of the total Zn. A stepwise linear regression revealed that total carbon, eCEC, pH and total sulfur accounted for 70% of the variance of available Fe, 62% of available Cu, 59% of the variance of available Zn, and only 19% of the variance of available Mn. The high correlation between available Fe and total carbon indicate that most of iron was organically bound. Cu was the heavy metal predominant on exchange sites, followed by Mn, Zn and Fe. Highly significant correlation ($P<0.01$) between the bioavailable and exchangeable forms of the same metal were obtained. Most of the variance of exchangeable Cu, Mn and Zn was accounted for eCEC followed by total carbon, pH and total sulfur. In the soluble fraction of the soil metal concentration followed the order Cu> Zn> Fe and Mn, Ni, Cd, Cr and Pb were not detected. The low Fe concentration in the soluble fraction was explained by the low solubility of Fe compounds, causing precipitation of hydroxides, which resulted in low correlation of Fe and any of the soil properties (Alvarez et al., 2003).

The Fankou and Lechang Pb/Zn mine tailings of China contained elevated concentrations of total and DTPA extractable Pb, Zn and Cu. Lechang tailings contained the highest total Cu (198 mg/kg), Zn (7607 mg/kg) and Fankou tailing contained the highest total Pb (5686 mg/kg). DTPA extractable Pb (219-269 mg/kg), Zn (249-326 mg/kg) and Cu (6.95-10 mg/kg) concentrations in tailings were similar ($P>0.05$) among the tailing samples and significantly higher than those of normal soil (Pb 6.82, Zn 3.79, Cu 1.10 mg/kg) (Shu et al., 2002).

Metal Accumulation in Plants Growing on Metal Enriched Soil

A pilot scale study conducted on the Fe tailings of Noamundi, Tata Steel by Maiti and Nandini (2005) reported that nine plant species could grow naturally on the Fe tailings, out of which four species namely, *Borhevia repens, Oxalis corniculata, Blumea lacera* and *Avera aspera* were analysed for total metal contents in the whole plant. The total metal contents in the natural vegetation varied widely between 1530-8412 mg Fe kg^{-1}, 17-102 mg Mn kg^{-1}, 28-110 mg Zn kg^{-1}, 10.8-18.8 mg Cu kg^{-1}, 5.2-35.8 mg Pb kg^{-1}, 12-32 mg Ni kg^{-1} and 5.5-31.8 mg Co kg^{-1}. Maximum accumulation of Fe was found in *Oxalis* (7442 $mgkg^{-1}$) whereas Mn and Zn were observed maximum in *Blumea lacera* (88 $mgkg^{-1}$) and *Avera aspera* (109 $mgkg^{-1}$) respectively. The variation of BAC (*Biological accumulation coefficient = total metals in plants/DTPA metals in soil*) for plants growing in the Fe tailings indicated that Fe was the element most easily absorbed by the plants. An absorption sequence was in the order of Fe>Ni>Pb>Zn>Cu>Mn> Co.

A significant correlation was observed between the $CaCl_2$ extractable metals in soil solution and Chinese cabbage (*Apium graveolens* L. ssp. *perkinensis)* grown on metal contaminated soil of northern China. An empirical model was developed to express the combined effect of soil properties on the phytoavailability.

$$\log [M_{root}] = a + b \log [M_{soil}] + c \text{ OM} + d \text{ pH} + e \text{ CEC} + f \log [M_{extra}]$$

where $[M_{root}]$ and $[M_{soil}]$ = total metal concentration in plant roots and soils respectively, $[M_{extra}]$ = metal concentration in the extractable soil fraction, and *a-f* = coefficients determined with statistical regression.

The stepwise multiple regression analysis demonstrated that the phytoavailability of trace elements strongly correlated with the extractable fraction by $CaCl_2$, total metal concentrations soils, and soil pH, OM and CEC. That model can describe 75-95% of the variability of metal uptake and r^2 values ranged from 0.741 to 0.954, which were much better than the single correlation analysis. For cerely (*Apium graveolens* L. ssp. *chinensis*) and cole (*Brassica campestris*), a strong correlation was observed for Cr, Ni, Zn, Cu, Cd, La, Ce, Pr and Nd whereas for spinach and Chinese cabbage, howewer, a positive correlation was only observed for Fe and Zn metals, respectively (Wang et al., 2004).

Twenty four plant species comprising 16 genera and 13 families, grown on degraded soils of Sao Domingo mine (south east of Portugal) were analysed for Ag, As, Cu, Ni, Pb and Zn. Pb concentration in plants was rather high for some species, varying from 2.9-84.9 mg/kg dry weight. The maximum Pb concentration was found in the aerial parts of *Juncus efusus*. Other semi-aquatic species sampled in the mining area like *Juncus conglomeratus* and *Scirpus holoschoenus*, showed high accumulation of lead in their tissue. Pb above 20 mg/kg DW was found in the leaves of three species of *Cisius*, typical mediterranean shrubs known for their tolerance to drought and low nutrient availability. As (arsenic) concentration in plant tissues ranged from 0.3-23.5 mg/ kg DW. Maximum As was found in *J. conglomeratus*, *Thymus mastichina*, *J. efusus* and *S. holoschoenus*. As and Pb were the most toxic metals found in the study area and the same assemblage of plants seem to better tolerate them. Semi-aquatic plant species from the *Juncaceae* family showed the highest content of both metals. A few trees, *Eucalyptus*, *Quercus* and *Pinus* species, were found in the contaminated area showing accumulation of different metals in the aboveground tissues (Freitas et al., 2004).

Despite the chemical limitations, various species of vegetation were found growing on the dump of abandoned mine in Galicia (NW Spain). The concentration of heavy metals in plants varied widely between 150-900 mg Fe/kg, 84-2069 mg Mn/kg, 20.5-106 mg Cu/kg and between 35-717 mg Zn/kg, taking into account all of the plant samples analysed. The concentrations of Fe in two herbaceous species studied, particularly *Festuca* sp., were higher than in tree and bush species. Of the tree species studied, the highest Fe concentration was found in *S. atrocinerea* and the lowest in *F. alnus*. *Q. robur* and *F. alnus* exhibited higher Fe concentrations in leaves than in twigs, whereas the opposite was true for *S. atrocinerea*. The highest concentrations of Mn were found in tree species, particularly in *E. alnus*, whereas lowest values of this element corresponded to *Festuca sp*. The opposite trend was observed for Fe concentrations, suggesting a possible interaction between these two elements. *Festuca* sp. was found to accumulate highest concentration of Cu, followed by *Blechnum speciant*, with the shrub and tree species showing much lower levels, similar to each other. In general terms, the species with the highest contents of Cu were those with the highest concentrations of Fe and the lowest of Mn. In *S. atrocinerea* and *Q. robur*, the Cu concentrations in leaves and twigs were similar, whereas in *F. alnus*, the leaves contained the higher levels. Levels of Zn in *S. atrocinerea* were much higher than in the other plant species. The same species accumulated most Zn in leaves, whereas *Q. robur* appeared to accumulate more in the shoot and *F. alnus* contained similar amounts in both parts. The Zn concentrations in plant samples were within the range (27-150 mg/kg) considered as normal by Kabata-Pendias and Pendias (1984), except those of *S. atrocinerea* in which both leaf and shoot contents were excessive or toxic (Alvarez et al., 2003).

A field trial was conducted to compare growth performance, metal accumulation of Vetiver (*Vetiveria zizaniodes*) and two legume species (*Sesbania rostrata* and *Sesbania sesban*) grown on the Pb/Zn tailings amended with domestic refuse and/or fertilizer. It was revealed that domestic refuse alone and the combination of domestic refuse and artificial fertilizer significantly improved the survival rates and growth of *V. zizaniodes* and two *Sesbania* species, especially the combination. However, artificial fertilizer alone did not improve both the survival rate and growth performance of the plants grown on tailings. Roots of these species accumulated similar levels of heavy metals, but the shoots of two *Sesbania* species accumulated higher (3-4 fold) concentrations of Pb, Zn, Cu and Cd than shoots of *V. zizaniodes*. Most of the heavy metals in *V. zizaniodes* were accumulated in roots, and the translocation of metals from roots to shoot was restricted. Intercropping of *V. zizaniodes* and *S. rostrata* did not show any beneficial effect on individual plant species, in terms of height, biomass, survival rate, and metal accumulation (Yang et al., 2003).

Conclusion

High metal concentrations and soil acidity represent primary limiting factors for plant growth on mine spoil/ tailings. Metals like Cu, Zn, Ni, Pb, Cr, As, Cd and Co cause toxicity problems in mine tailings/waste due to the presence of sulphide ores, which lowers the pH of the substrate due to its oxidation. Sometimes these metals are present beyond the tolerance limits of the plants. Thus, evaluation of toxic metal content in metal enriched soil in terms of total, bioavailable, exchangeable or soluble fraction is a good tool for potential risk assessment, due to the different and complex distribution patterns of metals among various chemical species or solid phases. Plant species found in metal enriched soil take up metals and eventually accumulate them. The bioavailability index are calculated by considering both bioavailable metals fractions (DTPA) as well as total metal contents with respect to the total metal accumulation in plant tissues. Thus, identification and thorough analysis of plant species grown on metals contaminated soil is an effective method for selecting potential plants to be used for reclamation purpose. Adding organic amendment is essential to facilitate the effective establishment and colonization of these pioneer plants. They can eventually modify the habitat and render it more suitable for subsequent plant communities. Planting of different grass species, rotating with legumes and native species will be able to reclaim soil fertility and accelerate ecological succession. In abroad, countries like China, Portugal, Spain, Italy, Ireland have been doing extensive research on the phytoremediation of metal contaminated site particularly Cu tailings, Pb/Zn tailings whereas in India, researches have just started.

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