

Bioremediation of Heavy Metal-polluted Environments through Compost Amendments and Composting Processes

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ABSTRACT

Pollution is a non-desirable consequence of most of anthropogenic activities. Contaminants accumulate in waters, sediments and soils, showing a high potential for causing damages in the ecosystems. Among these pollutants, heavy metals present the special feature of being non biodegradable, which makes them persistent in the environment. This fact determines the nature of the technologies used for the reclamation of polluted environments, since extraction and stabilization or immobilization are the only viable strategies. The former are generally carried out *ex situ*, resulting in high costs and negative affectation of the polluted area. On the contrary, stabilization techniques can be carried out *in situ*, which made them economically more attractive, although they are more time consuming and tend to cause some uncertainty. They are containment technologies based on the use of plants and/or soil amendments in the polluted environment to reduce metal toxicity by metal fixation in the soil as hardly-available forms. The input of organic matter causes a double effect on both the physico-chemical properties and the associated microbiota of the polluted area, which in turn contribute to alter the physical form of heavy metals and reduce their mobility and bioavailability. Among the different materials tested, compost has been referenced as one of the most valuable substrates. Compost increases the chemical status of the soil, promotes microbial populations and their activity and favors the re-establishment of vegetation. Composting may also be a useful strategy, although available information is scarce. A better understanding of mechanisms of action and the promoted effects is needed for its implementation as a usual technique for the reclamation of heavy metal-polluted areas, both in relation to composting and compost amendments.

Keywords: bioavailability, biostimulation, heavy metal decontamination, organic matter

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INTRODUCTION

From an ecological point of view, the term "heavy metal" refers to any metallic element potentially harmful for the environment and resistant to biodegradation (Sarma *et al.* 2011). Regardless of the vital role some of them play on account of their participation in biological functions (Babula *et al.* 2008; Nagajyoti *et al.* 2010), all of them has the potential to cause toxic effects in living organisms at low (non-essential metals such as Cd, Pb, As or Hg) or high (essential metals or trace elements such as Co, Cu, Cr, Fe, Mn, Ni or Zn) concentrations. Nevertheless, the toxic potential depends on the oxidation state, chemical form, dose, mode of exposure and the binding capability the heavy metal shows (Beyersmann and Hartwig 2008; Sinicropo *et*

al. 2010). Adverse effects on human beings, animals and plants have been reported (Beyersmann and Hartwig 2008; Smith et al. 2009; Berny et al. 2010; Guitart et al. 2010a, 2010b; Gundacker et al. 2010b; Nagajyoti et al. 2010; Soderland et al. 2010). Microorganisms, a really influential community on biogeochemical cycles and ecosystems productivity, can be profoundly altered by HM accumulation either (Hinojosa et al. 2005). Taking into account the serious risk they involve for living organisms and the impossibility of being chemically or biologically degraded (Pérez de Mora et al. 2006a), different alternatives have been proposed over the last decades to promote their removal or containment, being those of biological nature one of the most effective (Park et al. 2011).

Heavy metals occur naturally in the Earth's crust. Wea-

thering processes, as well as wind-blown dusts, volcanic eruptions or wood fires are main responsible for the release of metallic elements in the environment from natural sources (MacKenzie and Canil 2008; Shcherbov et al. 2008; Balabanova et al. 2011). Nevertheless, availability of elements from this origin, especially in soils, is scarce because of low solubility and the presence of forms that cannot be assimilated by most of the living organisms (Park et al. 2011). But HM pollution can be originated not only by natural sources but anthropogenic activities. Actually, activities like agriculture or industry are major contributors to heavy metal accumulation in the environment, as well as domestic effluents or combustion processes (Nagajyoti et al. 2010). In agriculture, the use of fertilizers and pesticides favors the input of HM in soils, although it should not be undervalued the contribution of irrigation practices with polluted waters (Singh et al 2010). Industrial sources such as mining, foundry and refinement, as well as some derived activities, release relatively high levels of HM to the environment (Sinicropi et al. 2010). Domestic effluents include either untreated or mechanically waste waters and wastes that, incorporated into effluents, are dumped into the sea, rivers o lakes (Nagajyoni et al. 2010).

Different strategies have been proposed to mitigate the deleterious effect that HM cause on those environments in which concentrations exceed the natural threshold, mainly soils, as the ecosystems where HM show higher persistence capacity (Lasat 2002). Since HM cannot be degraded, all the applied methods lie in their extraction or containment. In both cases, ex situ and in situ applications can be considered. Because this last methods are usually expensive and may cause some structural and functional disturbances, especially in soils (Pérez de Mora et al. 2006a; Helmisaari et al. 2007), in situ strategies are preferred. Nevertheless, drawbacks such as they are time consuming and tend to show some uncertainty have been attributed to these techniques (Farrell et al. 2010b). Among in situ strategies, physical, chemical and biological methods can be differentiated. Despite they are applied in some extension, physical (soil vapor extraction, soil leaching, soil washing, soil flushing, electrokinetic or absorbent fixation) and chemical techniques (chelate extraction) have proved not to be completely effective, either by the impossibility to reduce toxicity of HM, the potential contamination of other associated ecosystems or by the use of reagents with potential to pollute o negatively affect soil quality (Virkutyte et al. 2002; Neagoe et al. 2009; Shi et al. 2009). Biological reclamation of HMs polluted soils includes animal remediation (earthworms), phytoremediation and microbiological remediation. The use of earthworms in the decontamination of affected soils is marginal, since their capacity to accumulate HM is poor because of both their low specific surface area and population and the lack of feasible methods to collect them (Wu et al. 2010). On the contrary, phyto and microremediation are increasingly gaining attention on account of their efficiency and the wide range of HM that can accumulate, as well as their consideration as clean and non-environmentally disruptive technologies (Wei et al. 2004; Wu et al. 2010). Both methods can act in synergy and take advantage of factors that potentially stimulate the biological activity of soils. Among these factors, the incorporation of organic amendments into soil has been proved as one of the most successful strategies regarding bioremediation improvement (Clemente et al. 2007a; Pardo et al. 2011), since metabolic functions of microorganisms and higher plants are usually enhanced by organic matter (Park et al. 2011) by means of better soil characteristics and plant growth conditions, and microbial proliferation (Fornes et al. 2009). Nevertheless, some caution should be took in order to avoid negative affectations of both soil and biota (Zubillaga and Lavado 206; Bastida et al. 2008), as well as non-desirable effects on HM bioavailability (Santibáñez et al. 2008).

Composting is considered as one of the most effective methods for the valorization of organic wastes nowadays. The transformations that microorganisms carry out on these materials, as well as the physico-chemical modifications that take place during the maturity stage, originate most of the times a biologically stable material, with high levels of humified organic matter and low HM contents (Alburquerque *et al.* 2010; Lopes *et al.* 2011) when the process is properly managed. These high quality composts are useful not only for the improvement of physical, chemical and biological soil properties (Fagnano *et al.* 2011; Ozores-Hampton *et al.* 2011) but for the reclamation of HMs polluted soils (Pérez de Mora *et al.* 2006a; Mahmoud 2011).

This review focuses in the outstanding aspects to be considered when compost amendment is used as the main strategy for the reclamation of HM contaminated soils. Either direct or indirect effects, as well as the mechanisms involved on every case will be discussed and compared with other methods.

HEAVY METALS IN SOILS: ABIOTIC INTERACTIONS

The soil is a complex heterogeneous medium in which mineral, organic, aqueous and gaseous phases coexist and create the proper habitat for living organisms. Mineral phase is mainly composed of silicates of aluminum, iron, calcium, magnesium and many different elements depending on the nature of the specific regional composition of Earth crust, environmental conditions and management strategies. This phase is major responsible for the soil type classification (sand, silt, clay, loam, etc.). The organic component comes from animal and vegetal material, which is microbiologically decomposed. Aqueous portion make pos-sible life and chemical reactions. These activities, together with atmospheric gases, produced the formation of the gaseous phase. The coexistence and the interactions among these phases lead to a dynamic system in which characteristics changes in response to variations either in physico-chemical properties and biological behavior. As a soil constituent, HM are affected by these modifications. Alterations in pH, organic matter content, redox potential or microbial structure affect HM mobility and bioavailability and determine the natural remediation capacity of soils (Neagoe et al. 2009; Farrell et al. 2010b).

Soils can interact with HM through different processes, with adsorption, and precipitation being the most important and methylation/demethylation as alternative chemical mechanism.

Adsorption and complexation

Adsorption from the aqueous to the solid phase is the most influential process on bioavailability of HM in soils (Fontes and Santos 2010). This mechanism implies the formation of surface complexes between the HM and a sorbent, both by non-specific (displacement of like-charged ions and establishment of electrostatic forces) and specific methods (formation of chemical covalent bonds between the solute and functional groups on the sorbent) (Park *et al.* 2011). This last mechanism results in higher adsorption capacity than expect just from the soil cation exchange capacity (CEC) and, together with some other factors, accounts for high sorption levels in soils with low CEC values (Sipos *et al.* 2009).

Soil HM adsorption capacity depends on pH, CEC, organic matter content, properties of the clay fraction, ionic strength of the solution, concentration of some metallic oxides and characteristics of the metal (Fontes and Santos 2010). Although a single factor rarely may explain the capacity of a specific soil to adsorb HM, CEC and, especially, pH have been proved as the most influent factors in most cases (Vega *et al.* 2010; Zeng *et al.* 2011). An increase in the soil pH leads to a higher availability of dissociated functional groups in the organic matter (carboxyl, phenolic, carbonyl and hydroxyl groups), which usually results in an increased affinity for metal cations (Park *et al.* 2011). Some of these functional groups show more than one zone in which HM can be adsorbed, forming multi-dentate com-

 Table 1 Microbial mechanisms involved in HM transformation (Gadd 2010).

Solubilization	Immobilization
Chemolithotrophic leaching	Biosorption
H^+ , Fe (III), SO_4^{2-}	Metal-binding peptides, polysaccharides and other extracellular polymeric substances,
Chemoorganotrophic leaching	cell wall and other structural biomolecules, metabolites
H ⁺ , siderophores, organic acids, metabolites	Intracellular accumulation
Rock and mineral bioweathering and biodeterioration	Transport phenomena, permeation, organellar localization, intracellular precipitation and sequestration, mineralization
	Biomineral formation
Biocorrosion of metals	Organic precipitation (oxalates), inorganic precipitation (carbonates, phosphates, oxides, hydroxides, sulfides), nanoparticulate biominerals, biomineralization
Redox mobilization	Redox immobilization
$Fe(III) \rightarrow Fe(II)$	$Mn(II) \rightarrow Mn(IV), Fe(II) \rightarrow Fe(III)$
$Mn(IV) \rightarrow Mn(II)$	$Cr(VI) \rightarrow Cr(III), Ag(I) \rightarrow Ag(0)$
$Hg(II) \rightarrow Hg(0)$	$Au(III) \rightarrow Au(0), Pd(II) \rightarrow Pd(0)$
$Se(0) \rightarrow Se(IV), Se(VI)$	$U(VI) \rightarrow U(IV), Tc(VII) \rightarrow Tc(IV)$
$Pu(IV) \rightarrow Pu(III)$	$Te(VI), Te(IV) \rightarrow Te(0)$
	$Se(VI), Se(IV) \rightarrow Se(0)$
Methylation	Metal sorption to biogenic minerals
$\text{SeO}_3^{2-}, \text{SeO}_4^{2-} \rightarrow (\text{CH}_3)_2\text{Se}, (\text{CH}_3)_2\text{Se}_2$	Mn and Fe oxides, sulfides
$\text{TeO}_3^{2-} \rightarrow (\text{CH}_3)_2\text{Te}$	Metal(oid) nanoparticles
(CH ₃) _n AsH _{3-n} , n=1,2,3	Au(0), Ag(0), Se(0), Pd(0), UO ₂
CH_3Hg^+	

plexes with more stable bonds. Humic and fulvic acids are the most important natural ligands for the formation of complexes with HM (Karpukhin and Bushuev 2007), although when they are present in high proportion in soil may reduced the extraction potential of anthropogenic chelants applied in phytoremediation processes (Yip *et al.* 2010).

Precipitation

Anions such as sulfate, carbonate, hydroxide, phosphate or sulfide promotes the immobilization of HM through the formation of non-soluble compounds when concentration of HM is significant and pH is high (Porter *et al.* 2004), although sulfide acts over a broad pH range when reducing conditions are dominant (Park *et al.* 2011).

Co-precipitation as salts is also possible, mainly in the presence of Fe, Mn and Al oxyhydroxydes (Kumpiene *et al.* 2008). In such cases, metals are immobilized at high pH values by sorption in the oxides that then precipitate in carbonate (Petrovic *et al.* 1999). This mechanism avoids further metal extraction by application of chelants, while chemically sorbed metals are affected by such amendments (Yobouet *et al.* 2010).

Methylation/demethylation mechanism

Although it cannot be considered as a primary mechanism on account of the levels of HM affected, methylation seems to be important in processes of volatilization of some HM (As, Hg, Sn or Se). Despite this is a basically biological phenomenon, chemical methylation can contribute in some extent to the process (Park *et al.* 2011) especially in relation to Hg. Thus, methylcobalamin, methyltin compounds, small organic molecules (acetic acid) and, above all, humic matter are potential methyl donors for Hg (Gardfeldt *et al.* 2003). This Hg-methylation processes gain importance in relation to other modification mechanisms at soil acid conditions (Qiu *et al.* 2005).

HEAVY METALS IN SOILS: BIOLOGICAL INTERACTIONS

Despite the cytotoxic effects they could exert in living organisms, some HM plays important roles in the metabolisms of microorganisms, plants and animals when are present in the right concentration. In soils, HM concentrations higher than those demanded by living organisms can alter both the microbiota and the vegetation. Microorganisms may be affected not only in their population size, but in their diversity and activity (Kavamura and Esposito 2010), which in turn influences decomposition of soil organic matter and soil respiration (Haferburg and Knothe 2007). On the other hand, plants suffer from oxidative stress and are unable to carry out some metabolic activities on account of the incorporation of HM into bioactive molecules (Babula *et al.* 2008). Nevertheless, both microorganisms and plants have developed some strategies to tolerate and even detoxified HM. These capacities can be successfully applied for the bioremediation of polluted soils.

Microbial modifications on HM bioavailability

Microorganisms show the ability to carry out processes that promote both mobilization and immobilization of HM, thus influencing the balance between soluble and insoluble forms (Gadd 2004) (**Table 1**). Both mechanisms are of interest regarding the preservation of soil as a healthy habitat for living organisms, since mobilization makes easier the removing of HM and immobilization contribute to reduce their bioaccesibility (Gadd 2004; Wiatrowski and Barkay 2005).

Microbial mechanisms for HM mobilization include leaching, redox reactions and methylation, as well as bioweathering and biocorrosion processes. Bioleaching can be carry out by both autotrophic and heterotrophic microorganisms (Narayan and Sahana 2009). In the first case, ironand sulfur-oxidizing bacteria directly solubilize metal sulfides and, indirectly, by means of acidification, other metal compounds (Chenand Lin 2010). Heterotrophic microorganisms act through the liberation of protons, organic acids or siderophores that promote metal solubilization via acidification and formation of complexes. It is of special relevance in phosphate- and sulfate-containing minerals and in environments with high pH values (Gadd 2000). Both strategies have been applied either in biomining and bioremediation (Petrisor *et al.* 2007; Blais *et al.* 2010).

Some HM can be mobilized through microbial redox reactions, mainly those performed by dissimilatory reducing bacteria. In such cases, Fe(III), Mn(IV), Se(VI), Cr(VI) or As(V) act as terminal electron acceptors and are transformed into more soluble forms (Gadd 2004; Babechuk *et al.* 2009). Moreover, those reactions which involve oxidized forms of Fe and Mn as oxides may also contribute to the release of other HM that are strongly adsorbed to the oxides (Van Laer *et al.* 2010). The incorporation of humic substances into soil may favor this last activity since they provide the electrons needed for the redox process (Bauer and Blodau 2006).

Biomethylation processes may affect the release of some HM, as in the case of Pb, Cd, Hg, Se, Te, As or Sb (Pongratz and Heumann 1999; Chasteen and Bentley 2003; Frohne *et al.* 2011). Both bacteria and fungi are able to transfer methyl groups to these metallic elements, either in aerobic and anaerobic conditions. Some of the aerobic microorganisms promoting this alkylation reaction are *Penicillium*, *Alternaria* or *Pseudomonas*, while clostridia, methanogens and sulfate-reducing bacteria are among those prokaryotic genera that carry out the same process in anaerobic conditions (Gadd 2010).

Microorganisms, as well as other living organisms, enhance metal mobilization from rocks and minerals mainly through biochemical mechanisms. The excretion of organic acids and other metabolites, together with the CO₂ released from respiratory metabolism, promote acid attacks on mineral surface that result on the alteration of their properties in different extent, including complete dissolution (Gadd 2007). Mycorrhizal fungi are considered as the most effective microorganisms in bioweathering (Birkefeld et al. 2006). Biocorrosion, which is related to natural and anthropogenic habitats, refers to the deterioration of metals accelerated by microbial surface colonization through biofilms. Microorganisms included in these biofilms act by means of either metabolites excretion such as organic and inorganic acids and volatile compounds, as well as enzymes, among them catalases, peroxidases and superoxide dismutases (Beech and Sunner 2004). Bacteria involved in corroding metal surfaces mostly belong to the sulfate-reducing bacteria, sulfur and manganese-oxidizing bacteria, iron oxidizing/reducing-bacteria and bacteria secreting organic acids and slime, all of them present in naturally occurring biofilms (Beech and Coutinho 2003).

Processes that lead to immobilization generally reduce the bioavailability of HM in soils, although modifications in environmental conditions may alter the equilibrium and return metals to aqueous phase. Microorganisms can immobilize HM through different actions, accumulation being one of the most important. Two different mechanisms must be distinguished regarding accumulation: biosorption and intracellular accumulation (Ledin 2000). The former refers to the capacity of microbial cells to bind metal species depending on their surface characteristics, mainly the presence of groups such as phosphoryl, amine, hydroxyl, sulfhydryl and carboxyl groups that are integrated into structural molecules, or extracellular substances like exopolysaccharides (Table 2). The complexity of microbial surface in relation to other sorbents of inorganic nature in soils and its higher adaptability to changeable conditions, make them better sorbent agents (Perdrial et al. 2008). Although both Gram negative and Gram positive bacteria have shown be effective as biosorbents, the former seem to be more adequate on account of the characteristics of their cell wall (Joo et al. 2010). In the case of fungi, chitin and derivates play the most important role in biosorption processes (Gadd 2004). Taking into account metal sorption to external surfaces is a mostly metabolism-independent process, nonliving biomass can be used with no detrimental effects in comparison to living cells. On the contrary, intracellular accumulation involves active uptake into the cytosol, a process which is energy-consuming and dependent of transport systems with varied affinity and specifity (Das and Guha 2009; Ma et al. 2009). Inside the microbial cells, properties of the HM and microbial characteristics determine further reactions, among them precipitation, location within intracellular structures or organelles, translocation, reduction or binding to specific molecules (Gadd 2004; Edwards and Bazylinski 2008).

Biomineralization, a process in which different living organisms are involved, is other mechanism by which microorganism promotes HM immobilization (Dove *et al.* 2003). Biominerals, with similar structure to those originated from geochemical processes, can be formed as a consequence of microbial activity. Two different processes

Table 2 Functional groups in bacterial surface for metal-binding (Haferbug and Kothe 2007).

Functional group	Location	Microorganism
Carboxyl	Lipopolysaccharide	Pseudomonas aeruginosa
	Peptidoglycan	Escherichia coli
	Peptidoglycan	Bacillus subtilis
Amine/imidazole	Polypeptide	Bacillus subtilis
	Polypeptide	Klebsiella pneumoniae
Thiol	Phytochelatins	Escherichia coli GMO
	Metallothioneins	Ralstonia eutropha GMO
Phosphoryl	Lipopolysaccharide	Escherichia coli
	Teichoic acid	Bacillus subtilis
	Phospholipids	Bacteria

have been described differing in the degree of control exerted by microorganisms. In the so-called biologically controlled mineralization, microbial cells directly control the process, since mineral particles act as cellular structure. This is the case of magnetosomes (Posfai and Dunin-Borkowski 2009). On the contrary, in the most common biologically induced mineralization, modifications in the environmental conditions caused by microorganisms promote the formation of minerals (Gadd 2010). Redox transformations, sorption processes or precipitation reactions are major responsible for this modifications, with sulfide as the most important extracellular metabolite for the formation of metals (Almendras et al. 2009). Additionally, microbial surface, through biosorption mechanisms, provide sites for the initiation of the nucleation process and further mineral formation (Lloyd et al. 2008). Thus, even dead cells can promote biomineralization (Gadd 2010).

Apart from biomineralization, redox processes contribute to HM immobilization, since the reduction of the metal redox state usually decreases its mobility. Moreover, both processes, biomineralization and reduction, are sometimes associated. Thus, in sulfate-reducing bacteria, Cr(VI) may be reduced as an indirect consequence of the reaction between the produced sulfide and Fe²⁺. This phenomenon has been described for some metal-reducing bacteria, in which biomineralization and metal precipitation coexist (Roh *et al.* 2007). Other HM likely to be reduced by sulfate-reducing or dissimilatory Fe(III)-reducing bacteria are Co(III), Mn(IV), U(VI), Tc(VII) and Pd (II) (Roh *et al.* 2006; Li and Krumholz 2009).

Another immobilization process in which biogenic minerals are involved is sorption. Mn and Fe oxides can sequester different HM (Hennebel *et al.* 2009) even in a more efficient way than chemically originated oxides, since the former have larger specific surface areas (Miyata *et al.* 2007).

Plants and HM interactions

The accumulation of HM in soils up to toxic levels has favored the development of tolerant plants with adaptative strategies which enable them to survive in this polluted environment and even hyperaccumulate the toxic metals. This last ability has aroused the attention of scientists and in the last few years, remediation of HMs polluted soils with plants, the so-called phytoremediation, has emerged as an interesting technology on account of its low cost, efficiency, simplicity and non-environmentally disruptive character (Sarma 2011). Mechanisms by which plants detoxify HMs polluted environments are diverse (Table 3), phytoextraction being the most promising (Fig. 1) (Ghosh and Singh 2005), either for the efficiency of this specific clean-up methodology and for the possibility to recovery the metals from the shoots (Chaney et al. 2007) or to be applied for energy production (Van Ginneken et al. 2007). Furthermore, phytoextraction removes HM from soil, which is an additional benefit as unexpected alterations in environmental conditions might induce the gradual release of these toxic elements if they remain in soil, as in the case of immobili-

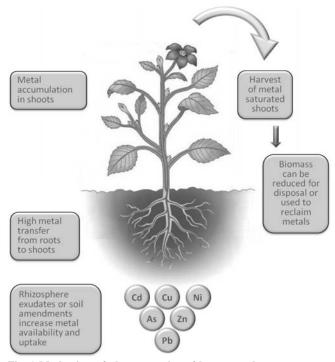


Fig. 1 Mechanism of phytoextraction of heavy metals. Source: Nascimento CWA, Xing B (2006) Phytoextraction: A review on enhanced metal availability and plant accumulation. *Scientia Agricola* 63, 299-311, with kind permission from Scientia Agricola, Paracicaba, Brazil.

Table 3 Mechanisms for heavy metals phytoremediation.

Mechanism	Definition	Applied in
Phytoextraction	Absorption of metals through the	Soils
	root system, where can be stored or	
	translocated to shoots	
Phytostabilization	Reduction of heavy metal	Soils,
	availability by means of the	sediments
	physical action of roots and their	
	influence on soil structure	
Phytoimmobilization	The interaction between plants and	Soils,
	microorganisms promote HM	sediments,
	immobilization through the binding	sludges
	to soil compounds, mainly lignin or	
	humus	
Phytovolatilization	Absorption of some HM by roots,	Soils
	further transformation into less	
	toxic forms and atmospheric	
	release	
Phytofiltration	Absorption or adsorption through	Aqueous
	plant roots (rhizofiltration) or	sources
	seedlings (blastofiltration) from	
	aqueous environments	

zation technologies. This is the so called "Time Bomb Hypothesis" (Brown et al. 1998).

Requirements for specimens to be applied in phytoextraction are: high capacity to absorb HM (preferably more than one) into the roots, potential for translocating HM from roots to the above-ground shoots, although some species are able to store them into the roots (Kavamura and Esposito 2010), fast growing and production of large quantities of plant biomass (Gamalero et al. 2009; Jadia and Fulekar 2009). Moreover, an external factor should be considered in relation to phytoremediation: microorganisms. The high nutritional status prevailing in the immediate vicinity of plant roots favors microbial growth to such level that the size of the population can be up to 1000-fold greater than standard microbial population in the soil (Glick 2010). In turn, microorganisms may enhance both root development and plant growth and health (Kuffner et al. 2010), as well as increase plant capacity to tolerate several environmental stresses (Kang *et al.* 2010) and alter HM phytoavailability (Karami and Shamsuddin 2010). Actually, in multiple-polluted environments, the combination of both plants and microorganisms (rhizoremediation) render better results than plants on their own (Jing *et al.* 2007).

In addition to stimulate microbial activity in the rhizosphere, the root exudates play a crucial role in HM mobility on account of their capacity for influencing acidification, chelation, precipitation, redox reactions, microbial activity and properties of both roots and rixhosphere (Kidd et al. 2009). Among them, low molecular-weight organic acids are the most well-established regarding this function. Metalchelating compounds and reducing molecules are either postulated as mobilizing agents, although this remains unclear and characteristics of these exudates are still unknown (Nascimento and Xing 2006). Nevertheless, some heavy metals are strongly immobilized in soils and show slow desorption rate, which is a major disadvantage for phytoextraction, since roots uptake metal preferably from the soil aqueous phase (Padmavathiamma and Li 2007). On the other hand, root exudates from some (hyper)-accumulating plants have been proved not to significantly affect HM mobilization in comparison to those from non-accumulating species, which point out the importance of soil properties such its buffering capacity (Kidd et al. 2009)

Phytostabilization and phytoimmobilization, the alternatives to phytoextraction when this last method is not a viable option (Alkorta et al. 2010) because of the prevalence of insoluble forms of HM or high clay contents (Kidd et al. 2009), leads to HM containment through primary mechanisms of precipitation in the rhizosphere and physical stabilization of soils, and absorption/ adsorption onto roots as secondary strategies (Mendez and Maier 2008). Thus, phytostabilization and phytoimmobilization are similar methodologies insofar as both of them reduce the biovailability of HM in soil without increasing the pollutant content in the aerial part of the plant, but they act through different mechanisms. While the former depends basically on the physical action of roots, the latter involves root activity also. Contrary to what is desirable in plants applied in phytoextraction, those species useful for phytostabilization this kind of processes should not hyperaccumulate metals into shoot tissues. Thus, the major objective for phytostabilization/ phytoimmobilization is not to remove HM from the polluted habitat but promote immobilization of HM up to safety thresholds for both human health and environment (Padmavathiamma and Li 2007). Other properties in demand for "phytostabilizing" plants are tolerance to high levels of HM and capacity for developing strong and large root systems. Additionally, these methods use to be applied in conjunction with organic soil amendments (Alkorta et al. 2010), which promote insolubilization of metals through the formation of complexes and the fixation in non-available soil fractions, increase the nutritional soil status even at long term time and contribute to the microbial richness (Clemente et al. 2007b; Park et al. 2011). Nevertheless, attention must be paid to the possibility of increasing HM content by adding some type of organic materials, which carry high levels of these pollutants. Municipal solid waste from non-source separated refuse, as well as its compost, has shown to be as the most problematic material regarding this concern. Thus, the application of fresh and composted organic amendments of good quality is a key point for HM remediation.

Some HM (As, Hg or Se) can exist as gaseous forms in nature. Phytovolatilization use the capacity of a reduced number of plants, which are able to absorb these metals and transform them into their gaseous forms and release them into the atmosphere. Advantages ascribable to this method are its low disruptive capacity, the limited management demanded after planting and the absence of polluted material to be disposed. Nevertheless, this is a polemic strategy, since the potential accumulation of toxic elements in the atmosphere is not a desirable trait on account of safety (Padmavathiamma and Li 2007), although studies point out the low rate in which phytovolatilization contributes to the atmospheric pool, mainly on account of their wide dispersion (Kotrba *et al.* 2009).

The last phytoremediation method, phytofiltration, is useful for the detoxification of polluted aqueous systems: groundwater, surface water and wastewater. Both plant roots and seedlings can absorb or adsorb HM through mechanisms including chemisorption, complexation, ion exchange, micro precipitation, hydroxide concentration onto the bio surface and surface adsorption (Gardea-Torresdey *et al.* 2004). The requirements for species to be used with this finality include, apart from those demanded in other phytoremediation technologies, the ability to act in low-concentration environments and accumulate at different nutrient levels (Khilji and Bareen 2008).

COMPOST AMENDMENT TO SOIL. EFFECTS ON HEAVY METALS

Heavy metals in soils can naturally be immobilized through sorption, precipitation and complexation mechanisms (Farrell and Jones 2010). Nevertheless, when metal concentration exceed the levels generally established as environmentally acceptable, this natural attenuation capacity of soils is not sufficiently efficient. Some strategies have been proposed to enhance or accelerate this capacity, among them both inorganic and organic amendments. The incorporation of these materials into soil exert a mostly positive influence in soil properties, which in a indirect way affect HMs mobility, and may modify directly the availability of these elements (Janoš et al. 2010). Actually, Adriano et al. (2004) propose the term "assisted natural remediation" to refer the improvement caused by soil amendment in natural biogeochemical processes that govern HMs mobility. Industrial waste or bio-products, sewage and paper mill sludge, gypsum and lime-rich industrial by-products, iron and aluminum industry derivates, phosphorus-containing materials, manganese oxides or clay minerals or compost are some of the products applied as contaminant immobilizing amendments (Kumpiene et al. 2008; Udeigwe et al. 2010). Although some detrimental effects on metals availability have been reported (Clemente et al. 2006; Mench et al. 2006; Del Moral et al. 2010), amendments mostly result in a reduced HMs mobility. Good management practices, as the adaptation of the amendment to soil properties and the metal or metals to be immobilized (Bolan and Duraisamy 2003; Fornes et al. 2009), may prevent these negative effects. Regarding compost, drawbacks are related to the potential incorporation of toxic components, including HMs, and the longevity of the treatment, which is a controversial question for most of the organic amendments (Burgos et al. 2010). However, benefits derived from compost incorporation to soil go beyond the potential damages that may cause when it is applied for the immobilization of HMs (Farrell and Jones 2010).

Direct modifications in HMs mobility caused by compost amendments

Compost incorporation into soil exerts a direct effect on both chemical and physical properties and, hence, structural modifications are expected. These changes have a direct influence on HM speciation. In general, HMs bioavailability tends to decrease when compost is applied to soil, as soluble forms are converted into less readily-available species (Walker *et al.* 2003). Nevertheless, a high level of dissolved organic matter (DOM) in the amendment, as in unstabilized non-composted materials, may favor metal complexation and increase mobility (Kiikkila *et al.* 2002; Ashworth and Alloway 2007). However, the specific effect of DOM depends on the heavy metal, since contrary results have been described for different elements (Bradl 2004). The influence of organic matter content on HMs mobility is mostly conditioned by the action of humic substances, which can reduce the availability of metals through the formation of stable chelates (Walker et al. 2004). Thus, the higher humification and stability degree in the compost, the higher potential for immobilizing HMs (Castaldi et al. 2005; de la Fuente et al. 2011). Carboxyl and hydroxyl groups in both humic and fulvic acids are major responsible for the establishment of chelates, with higher stability as pH increases on account of deprotonation phenomena and higher availability of negative charges (Wang and Mulligan 2009). Nevertheless, contrary effects have been described, since high pH values may either promote the formation of soluble metalhumate species or hinder the metal hydroxide production. Furthermore, this last process prevents the potential adsorption or coprecipitation onto and with the hydroxides of some HMs (Clemente et al. 2010). Thus, some studies report a double influence as a consequence of compost amendment, by which the concentration of free elements in soil water decrease but the content of complexed forms increase (Kiikkila et al. 2001; Clemente et al. 2003). However, the final effect mostly consists on a reduction of biotoxicity. Other traits to be considered in the impact that organic matter exert on HMs is the possible modification of soil redox potential, which can alter HM speciation (Doelsch et al. 2010) and the way in which compost is applied, since mulching surface seems to produce a better flushing of dissolved organic matter than the incorporation into the soil matrix (Hartley et al. 2010).

Composted organic matter show low levels of DOM and a high stabilization degree which, in turn, reduces its potential for metal leaching (Kumpiene *et al.* 2008). Probably, the high content of hydrophilic groups in DOM may be responsible for this greater binding-capacity (Zhou and Wong 2001).

Impact of compost addition to soil is heterogeneous, since results described in literature prove the dependency of effects on the type of compost and soil (Van Herwijnen *et al.* 2007; Farrell and Jones 2010). In general, the incorporation of compost to soil results in significant increases of pH, organic matter level and water content (Pérez de Mora *et al.* 2007). These characteristics affect HMs mobility, and favor metal conversion into less soluble and available forms (Alvarenga *et al.* 2009; Liu *et al.* 2009) (**Fig. 2**).

In comparison with other organic amendments, compost has shown a higher efficiency for reducing HMs bioavailability, which may due to the lower mineralization rate of mature compost and the more reactive nature of the organic components present in compost (Pérez de Mora et al. 2007). Thus, Burgos et al. (2006) described the higher influence of compost in reducing HMs bioavailability in relation to leonardite, while De la Fuente et al. (2011) reported a greater capacity of compost for decreasing metal solubility in relation to the non-composted material, probably on account of the higher pH values that compost promotes (Alburquerque et al. 2010). Beesley et al. (2010) found that concentrations of extractable metal forms were significantly lower in soils amended with green waste compost instead of biochar. Nevertheless, Walker et al. (2004) have reported higher level of extractable metals when compost amendment was applied to soil in comparison with fresh organic matter addition. The presence of unstable organic matter in the fresh material leads to a great rate of mineralization that results in less oxidizing conditions, which in turn hampers sulfide oxidation processes. In the case of compost, the higher stability of organic matter results in a negligible mineralization rate and a significant sulfide oxidation. Thus, higher pH values are promoted by fresh organic matter in comparison with compost in sulphide soils.

Regarding to pĤ, probably the most important factor in controlling HMs bioavailability (Gadepalle *et al.* 2009), compost in soil seems to demand a higher proton consumption, which promotes soil alkalinization (Hartley *et al.* 2010). As HMs solubility decreases as pH values are over 6 (Clemente *et al.* 2005), this effect of compost is strongly significant, especially in acidic soils where the modification of pH is a common practice aimed to reduce pollutants incidence (Adriano 2001). Actually, it has been established a

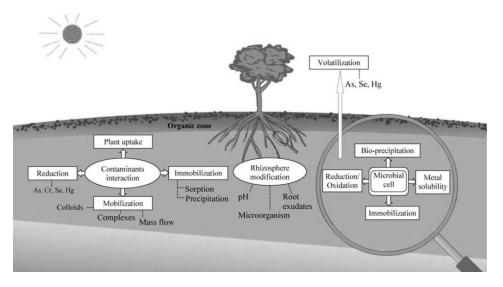


Fig. 2 Organic amendments influence on processes that rules heavy metal mobilization in soil. Source: Park JH, Lamb D, Paneerselvam P, Choppala G, Bolan N, Chung JW (2011) Role of organic amendments on enhanced bioremediation of heavy metal(oid) contaminated soils. *Journal of Hazardous Materials* 185, 549-574, with kind permission from Elsevier, Oxford, UK.

decrease of approximately 2-fold in HMs concentration in soil solution as a consequence of each unit of increase in pH (Pérez de Mora et al. 2006a). Nevertheless, great increases may exert detrimental effects on the growth of some specific plants which demand pH values under neutrality (Helmisaari et al. 2007). Thus, although the buffering capacity of soil use to prevent such impacts, a balance between the required pH increase for reducing HMs availability and the damage potentially caused to organisms and plants should be took and particular attention has to be paid to changes in pH following soil amendments in those cases in which these acidic plants are involved. In this sense, compost promotes modifications in pH high enough to immobilize HMs in a significant extension but not so high as to affect plant development (Castaldi et al. 2005). Mechanisms involved in pH increase include the release of OH- ions by ligand exchange processes, the incorporation of cations with basic nature (K^+) , Ca^{2+} , Mg^{2+}) and, in a lesser extension, carbon mineralization (Mkhabela and Warman 2005). As a result, the number of sites for adsorption increase and ionic metal forms with higher affinity for these sites are generated (Chen et al. 2010).

Indirect modifications in HMs mobility caused by compost amendments

The incorporation of organic matter into soil improves intrinsic soil properties and, therefore, plant growth and microbial activity. Since plants and microorganisms can be considered as two effective HMs immobilizing agents, the effect of compost must be analyzed not only because of its direct influence on HMs but for its beneficial effect on these organisms. On the one hand, compost amendments into HMs polluted soils generally result in an increase of the microbial biomass (Pérez de Mora et al. 2006a; Fornes et al. 2009). This effect is mostly attributed to a higher total organic carbon and water soluble carbon, as well as the microbial content present in the compost (Inbar et al. 2005; Ros et al. 2006; de la Fuente et al. 2011). Moreover, the ratio between microbial biomass and total organic carbon, which is considered as a good indicator of how reactive is the organic matter in soil, also show higher levels after compost amendments (Pérez de Mora et al. 2006b). Also, microbial activity is either affected by compost incorporation to HMs polluted-soils (Branzini et al. 2009). Firstly, microorganisms exposed to HM tend to show a lower efficiency in the utilization of organic C (Khan and Scullion 2002), and therefore a high organic matter input contribute to sustain a normal level of activity. Secondly, the properties of the organic matter contained in compost amendment may condition the prevalent microbial communities in soil (Alburquerque *et al.* 2010), despite the greater microbial diversity promoted by compost amendment, not just in comparison with untreated soils but with inorganic amended soils (Farrell *et al.* 2010a). Hence, the beneficial influence of compost on soil microbial population under HM stress, both quantitatively and qualitatively, lies on the combined action of different effects, among them pH modification, increased nutrient availability and incorporation of microbial biomass (Alburquerque *et al.* 2010).

Together with the promotion of both microbial population and diversity, compost incorporation to HMs polluted soils results in a higher microbial activity (Kiikkila et al. 2001; Pérez de Mora et al. 2005; Fornes et al. 2009), both for the addition of the intra- and extracellular enzymes that compost may contain and the possible stimulation of microbial activity. Moreover, the capacity of the organic matter in compost to immobilize HMs, limit the availability of these elements for interacting with substrates and enzymes (Tejada et al. 2008), since free forms of metals hinder enzymatic activity by combining with the substrate, the enzyme and even the enzyme-substrate complex (Madejón et al. 2001). The high stability and maturity of compost in relation to other organic amendments increase its efficiency for binding HMs, taking into account that humified materials (humic acids) content larger molecules and show higher aromaticity than immature amendments, with higher proportion of fulvic acids (Gondar et al. 2006). Both traits contribute not only to increase the number of groups involved in the binding reactions but to improve the structural properties of the binding sites (Christl et al. 2001), which results in a higher binding capacity for those materials with higher humic acid content, as compost (Quang and Yan 2010). Nevertheless, some others considerations should be taking into account, since interactions between metals and sorbent materials show different affinity rates depending on each one (Covelo et al. 2007). Thus, the election of a concrete material for remediating HMs polluted soil should be took having in mind which is the dominant metallic element.

Incorporation of compost to soil provides carbon and nutrients, which may in turn stimulate the activity of those microbial populations involved in HMs immobilization, such as sulfate reducing bacteria (Jong and Parry 2003; Van Roy *et al.* 2006). These bacteria demand a carbon source that acts as a electron donor and promotes growth and, at the same time, allow the activity of other microbial populations responsible for the removing of oxygen (Diels *et al.* 2002), since this process is only achieved under low redox potential conditions. Although some studies question the capacity of compost to support the activity of sulfate reducing bacteria (Gilbert *et al.* 2004), probably because of the high content in lignified materials, most of the reports point out the suitability of this substrate to fit the nutritional demands of sulfate reducing bacteria (Kaksonen and Puhakka 2007; Pagnanelli *et al.* 2008).

Other microbiological process that seems to be stimulated by compost is the reduction of Fe(III) to Fe(II). This chemical form is able to effectively reduce other heavy metals to less toxic forms, as happens with Cr(VI). According to Huang *et al.* (2010) compost is a most suitable amendment for this purpose than non composted material, on account of a higher electron-donating capacity derived from a greater humification degree. Also As methylation, an exclusively microbial process, is enhanced by compost amendments to soil (Hartley *et al.* 2010). A previous bioreduction of As(V) to As(III), which is stimulated by organic matter either (Dobran and Zagury 2006), is needed.

Microbial processes may be either of interest in phytoremediation methodologies (Shilev et al. 2009), especially when this is the first step in combined strategies in which available forms of HMs are further phytoextracted by (hyper)-accumulating plants (Kamnev 2003) or immobilization improves phytostabilization (Kuffner et al. 2010). The production of organic acids and other compounds by microorganisms (Arwidsson et al. 2010), mainly siderophores (Rajkumar et al. 2010), results in lowering soil pH and increasing HMs solubility, as well as higher availability of metal complexing ligands that promotes the formation of soluble complexes and metal uptake by acidification, chelation, precipitation, immobilization and redox processes in the rhizosphere. Either some plant growth promoting rhizobacteria and other microorganisms, which are resistant to relatively high concentrations of HMs, may enhance phytoremediation both directly through the mobilizing mechanisms previously cited and indirectly by improving fertility of polluted soils and stimulating plant growth (Karami and Shamsuddin 2010). These bacteria produce phytohormones such as auxins, cytokinins, gibberellins or ethylene (Perrig et al. 2007), as well as other secondary metabolites (enzymes. osmolites, biosurfactants, siderophores, nitric oxide, organic acids or antibiotics) that influence plant growth through different mechanisms, among them suppression of pathogenic microorganisms, tolerance to abiotic stresses, improved mineral uptake or associative nitrogen fixation (Ma et al. 2011). Since HMs negatively affect microbial activity (Oliveira and Pampulha 2006), all the processes that reduce HMs concentration in soil can potentially improve microbial growth and increase the content of the compounds produced during such growth. Compost amendment to soil promotes microbial activity not only as a consequence of the decrease in HMs bioavailability, but for the improvement of the soil properties (Pérez de Mora et al. 2006a; Park et al. 2011).

Phytoremediation can be also enhanced by the direct incorporation of organic matter (Karami and Shamsuddin 2010), although some studies describe the lower accumulation in plant tissues as a consequence of compost amendment to soil (Pérez de Mora et al. 2006c; Tandy et al 2009). This effect can be ascribed to different factors, both direct and indirect. Among the former, increases in soil pH and interactions with organic matter probably contribute to lower phytoavailability of HMs (Van Herwijnen et al. 2007), whereas the higher soil fertility results in the indirect restriction of metal uptake through block or precipitation caused by nutrient ions (Farrell et al. 2010b). The use of (hyper)-accumulating or excluding plants also affect the distribution of HMs into plant tissues. Thus, concentration of HMs is higher in shoots than in roots in (hyper)-accumulators, whereas the opposite trend has been observed in excluders (Kirkham 2006). This difference seems to be based on the development of adaptation strategies, since mechanisms for HMs tolerance by exclusion minimize HMs in the aerial parts by keeping them in the root tissues, controlling transport to the shoots, while (hyper)-accumulators fights against HMs by transport and accumulation in the vacuoles

of the leaves in non-toxic forms. It has been proposed that metal accumulation can act as a defense tool against pathogens in (hyper)-accumulators (Kukier et al. 2004; Poschenrieder et al. 2006). Metal protection is only possible if the metal is less toxic to the plant than to the parasite (Poschenrieder et al. 2006). On the other side, endophytic bacteria can reduce metal accumulation in roots and shoots (Madhaiyan et al. 2007). Despite this detrimental effect on phytoextraction capacity, plant yield and rooting depth use to be higher when compost is added to soil (Farrell *et al.* 2010b). As a result, the final balance of compost influence may be positive since the decrease in concentrations of HMs in plant tissues can be counteracted by the higher plant biomass (Pérez de Mora et al. 2006c). In this sense, combined strategies in which reduced compost amendment supplemented with plant growth promoting bacteria have proved to be successful in terms of amelioration of polluted soil and cost (Grandlic et al. 2008). Thus, strategies that improve soil properties and promote slight decreases in HMs solubility, just in the right extension to limit toxic effects of HMs on plants, stimulate biomass production growth and allow a significant uptake of metals. In this sense, compost can be considered as an interesting material to enhance both plant growth and metal uptake, especially in spoiled soils (Pedron et al. 2009).

In those cases where conditions do no permit the application of phytoextraction methodologies, and better results are expected by using containment strategies, soil properties should promote both HMs immobility and plant growth. Nevertheless, this last demand is often hampered by the negative characteristics of HMs polluted soils (Pérez de Mora *et al.* 2006c). Compost incorporation into soil contribute to improve these properties and (Frutosa *et al.* 2010), therefore, to enhance HMs containment (Adriano *et al.* 2004).

COMPOSTING vs. COMPOST AMENDMENT

Co-composting of soils contaminated with organic pollutants have been proved as a successful strategy (Ahtiainen *et al.* 2002; Namkoong *et al.* 2002), although some drawbacks have been observed depending of the properties of the contaminant and the degradation products (Semple *et al.* 2001). However, the application of similar strategies for the reclamation of soils polluted with trace elements is still an unexplored field.

Efficiency of compost in the amelioration of HMs polluted soils lies in a significant extension on the content of humified compounds this material provides. Thus, it could be interesting to test the capacity of humic substances to bind HMs as the humification process proceed in comparison to the previously formed humified matter of compost (Tandy et al. 2009). According to the results reported by these authors, co-composting of contaminated soil and organic wastes do not result in significant advantages regarding metal speciation or bioavailability and, taking into account the cost and logistic of co-composting, the absence of clear benefits they advise against its implementation. Nevertheless, it is worth notice that although final concentration of HMs in co-composted soils and sediments could be increased, mainly as a consequence of total matter reduction, the levels of bioavailable forms decrease (Niu et al. 2009; Yu et al. 2009), which is advantageous since HMs impact in soil is more related to their chemical species rather than their total concentration (He et al. 2009). Zeng et al. (2007) report that the bioaugmentation of the composting process result in even higher reduction in HMs bioavailability, which may be caused for both improving of the process and enhancing of the formation of chelates, as active functional groups in microbial surface are increased.

INCREASING HEAVY METAL SOIL CONTENT BY COMPOST AMENDMENTS

Different materials with high organic matter content can be satisfactory composted and successfully used as organic amendment. Nevertheless, the increasing content of pollutants in the raw material used as feedstock compromises the safety utilization of compost, especially for both agricultural and recreational soils (Farrell *et al.* 2010b).

In terms of heavy metals, most of the countries have stated regulatory guidelines which determine the maximal allowable HMs contents. Nevertheless, these regulations mostly refers to total content of HMs and do not take into account those aspects associated to speciation, which determine toxicity, mobility and bioavailability (Greenway and Song 2002). The metal composition of final product of composting depends on the raw material, the process and the geographical location (Iwegbue et al. 2007) and the distribution among the different potential forms depends on the way in which the process has proceed. As in other natural matrices, trace elements in compost can adapt different forms and be associated to different compounds: watersoluble and exchangeable forms, bound to organic molecules or co-precipitated with oxides, carbonates or phosphates. Water soluble and exchangeable forms show the higher bioavailability. Thus, the lower proportion of trace elements in these forms, the better quality of compost in relation to HMs.

Although total HMs content through composting use to increase as a consequence of the organic matter loss (Barker and Bryson 2002), at the end of the process partitioning profiles show a majority tendency to reduce levels of available forms and increase the fractions linked to humic and other organic substances (Singh and Agrawal 2008). Nevertheless, differences have been described depending on specific element and raw material. Taking this into account, heavy metal speciation during composting is rather difficult to predict, as many different factor are involved in final results (Farrel et al. 2009). Thus, while some studies report that the proportions of Cu, Zn and Pb tend to increase (He et al. 2009), which is hardly extractable and bioavailable, and Ni show a high tendency to form soluble species (Amir et al. 2005), others authors describe an increase in Zn and Pb bound to the easily-extractable fractions (Cai et al. 2007; Liu et al. 2007) and a reduction of Ni and Cu bioavailability (Wang et al. 2007). Then, amendment with municipal solid waste sometimes results in the increase of HMs soil concentration (Madrid et al. 2007). Nevertheless, has been referred to extensively in previous sections, compost incorporation into soil is an effective strategy not only for the bioremediation of polluted soils but for the reclamation of disturbed soils. The application of more efficient practices of waste separation prior to composting might reduce the content of trace elements in the final compost (Madrid et al. 2007).

CONCLUDING REMARKS

In last decades, public concerns relating to the ecological threats caused by heavy metal pollution have progressively grown as input levels into different habitats have increased up to levels that mean a serious risk to both environment and human beings. Anthropogenic activities, as well as inadequate use or residue disposal of the materials in which they are contained are major responsible for its accumulation. Remediation of such undesirable scenarios implies a challenge to the scientific community, which must offer responds to the commitment of providing strategies that alleviate these detrimental conditions and minimize the potential for causing dangerous effects. Among the different proposals, biological technologies have emerged as the most efficient according to the rate cost/effectiveness. Bioremediation, which involves the application of plants and microorganisms for the reclamation of polluted habitats, appear as a very advantageous methodology. Despite the unquestionable benefits derived from their application, drawbacks exist that limit its efficiency. Regarding this, practices that improve the performance of bioremediation are welcome. Particularly, the reclamation of soils polluted with heavy metals can be successfully promoted by the incorporation of organic matter and, specially, compost. Compost amendment to soil add stabilized and humified organic matter, which results in the improvement of soil properties and the stimulation of both microbial activity and plant growth. Thus, bioavailability of heavy metals is mostly reduced as a consequence of the better physico-chemical soil characteristics and the higher biological activity. Nevertheless, properties of the compost amendment must be adapted to the specific conditions of the soil in which it is going to be applied and quality standards have to be ensured, thus minimizing possible detrimental effects associated to inadequate applications or the use of low quality amendments.

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