

Fate of Heavy Metals Exposed to Composting Environments and Composts

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ABSTRACT

Heavy metal remediation of contaminated aqueous streams and soils is of great environmental concern. When present in excessive concentrations, heavy metals can become extremely toxic to the receiving bodies and pose serious health threats. Composting as a bioremediation technique offers the possibility to render less harmless various heavy metal contaminants using the natural biological activity of composting matrices due to the presence of bacteria, actinomycetes and lignolytic fungi. This review article presents an outlook on the speciation, immobilization mechanisms, uptake and fate of heavy metals present during the composting processes and when exposed to composts by essentially revisiting the essential biochemical and microbiological aspects of the composting process, and assessing the application of composting/composts in influencing the speciation and fate of heavy metals.

Keywords: heavy metals, fate, bioavailability, uptake mechanisms, bioremediation

Abbreviations: CC, complexing capacities; DOM, dissolved organic matter; DTPA, diethylene triamine pentacetic acid; FT-IR, Fourier transform infrared; FA, fulvic acid; HM, heavy metal; HA, humic acid; HS, humic substance; HoA, hydrophobic acid; HoN, hydrophobic neutral; HiB, hydrophilic base; HiA, hydrophilic acid; ISE, ion-selective electrode; MSW, municipal solid waste; MSWC, municipal solid wastes compost; OM, organic matter

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INTRODUCTION

Together with rapid industrial and economic development, a variety of anthropogenic activities have caused widespread environmental pollution of the globe (Ang *et al.* 2005). Organic pollutants such as pesticides and herbicides are now dispersed throughout the environment and can be highly refractory to biodegradation processes found in naturally occurring microorganisms (Martínez-Huitle *et al.* 2008; Sipma *et al.* 2010). In parallel, rapid industrialization and urbanization have resulted in the elevated emission of toxic heavy metals entering the biosphere. The term 'heavy metals', hereafter referred to as HMs, refers to metals and metalloids having densities greater than 5 g cm⁻³ and is usually associated with pollution and toxicity. Primary sources of pollution are from the burning of fossil fuels, mining and melting of metallic ferrous ores, municipal wastes, fertilizers, pesticides, and sewage sludge (Peng *et al.* 2006; Elouear *et al.* 2008). The most common HMs contaminants are: cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) (Lu *et al.* 2004).

The release of HMs in biologically available forms may damage or alter both natural and man-made ecosystems.

Some HMs ions are essential micronutrients for plant and human metabolism (Gamalero *et al.* 2009; Puig and Peñarubia 2009; Lokhande *et al.* 2010), and are natural substances found, usually at low levels, in soils. However, when present in excessive concentrations in soils and groundwaters, they can become extremely toxic to the receiving living micro and macro environments and pose serious health risks and problems (Khoshgoftarmanesh *et al.* 2009). Cadmium (Cd²⁺) is a non-essential HM which slowly accumulates in the body of living species, usually through the food chain (Srivastava *et al.* 2006; Zhao *et al.* 2011). Nickel (Ni²⁺) is also toxic, especially to activated sludge bacteria and the presence of Ni²⁺ has been reported to be detrimental to the operation of anaerobic digesters used in wastewater treatment plants. Cd²⁺ and Ni²⁺ ions are frequently encountered together in industrial wastewaters. Hence, it is essential to remove Cd and Ni from industrial wastewaters before transport and cycling into the nature environment.

The soil has been traditionally the site for disposal for most of the HMs wastes which need to be treated (Abou-roos *et al.* 2006). Cr in solutions mostly occurs as oxyacids and oxyanions of Cr⁶⁺ (Xu and Zhao 2007). Cr⁶⁺ is highly soluble, mobile and toxic with acute and chronic adverse

effects on warm-blooded organisms. Under laboratory conditions, Cr^{6+} has been found to have the greatest biological activity and also to be mutagenic, carcinogenic, and teratogenic to a wide variety of organisms. Nevertheless, HMs such as copper have been a much overlooked contributor to many health problems but they are reported to be a cause to anorexia, fatigue, premenstrual syndrome, depression, migraines and headaches, allergies, childhood hyperactivity. Therefore, HMs remediation of aqueous streams and soils is of special concern due to the recalcitrant, persistent and ecotoxic nature of HMs in the environment (Sud *et al.* 2008; Wang *et al.* 2011).

Conventional methods for the removal of the HMs ions from wastewaters, contaminated natural waters and soils include chemical precipitation (Aziz *et al.* 2008), electroflotation (Belkacem *et al.* 2008), ion exchange (Smara *et al.* 2007), reverse osmosis (Kurniawan *et al.* 2006; Huang *et al.* 2011) and adsorption onto activated carbon and biosorbents (Cimino *et al.* 2005; Wang and Chen 2006; Park *et al.* 2011). However, due to operational demerits, high cost of the treatment and the generation of toxic chemical sludges, greener technologies have been tried for a long time. A better approach than these traditional methods is to sequester or transform them to less innocuous substances (Vidali 2001).

Bioremediation is an option that offers the possibility to make less harmless various HM contaminants using natural biological activity (Vidali 2001; Harms *et al.* 2011). Bioremediation is the use of living organisms, primarily microorganisms, to degrade the environmental contaminants into less toxic and harmless forms. Contaminant species are transformed by living organisms through biochemical reactions that take place as a part of their metabolic processes, and the biodegradation/biostabilization of a compound is often a result of the actions of multiple organisms or bioaugmented microbial consortia (Berthe-Corti *et al.* 2007; Pant and Pant 2010). There are many well-established bioremediation technologies applied at contaminated sites (Khan and Anjaneyulu 2006; Harms *et al.* 2011). Bioleaching, biosorption, bioaugmentation, biostimulation, biopulping, biodeterioration, bioleaching, bioaccumulation, biotransformation and bioattenuation are being actively researched on and optimized in their environmental clean-up potential (Whiteley and Lee 2006; Lü *et al.* 2011).

One such green bioremediation technology is the application of composting and use of compost (Ceccanti *et al.* 2006; Tang *et al.* 2009). Composting matrices and composts are rich sources of xenobiotic-degrading microorganisms including bacteria, actinomycetes and lignolytic fungi, which can degrade pollutants to harmless compounds such as carbon dioxide and water (Ryckeboer *et al.* 2003), or alternatively provide for contaminant sequestration pathways. Hence, these microorganisms can also metabolize pollutants into less toxic substances and/or lock up pollutants within the organic matrix, thereby reducing the pollutant bioavailability to other vulnerable media. The success of a composting bioremediation strategy depends however on countless factors, of which the pollutant bioavailability and biodegradability potential are apparently more important (Semple *et al.* 2001). The objective of this review is to highlight, appraise and evaluate the recent developments in the remediation of media contaminated with HMs using the composting process and composts. The review is divided into two main sections namely (i) a discussion of the essential chemical, biochemical and microbiological aspects of the composting process, and (ii) the speciation, uptake, remediation and/or fixation of HMs in the composting environment. Composting being environmentally sound and benign holds opportunities for the advancement of the bioremediation technology and offers the prospect of stabilizing some of the most recalcitrant HMs in the modern global environment.

THE COMPOSTING PROCESS

Composting can be defined as the controlled biological de-

composition of organic substrates carried out by successive microbial populations combining both mesophilic and thermophilic activities, leading to the production of a final product sufficiently stable for storage and application to land without adverse environmental effects (Petiot and de Guardia 2004). Under optimal conditions, composting proceeds from the initial ambient state through three phases: (a) the mesophilic or moderate-temperature phase, which lasts for a few days, (b) the thermophilic or high-temperature phase, which can last from a few days to several months, and (c) the cooling and maturation phase which lasts for several months (Ghaly *et al.* 2006). This thermophilic stage is governed by the basic principles of heat and mass transfer and by the biological constraints of living microorganisms. Ryckeboer *et al.* (2003) have intensively examined the diversity and population densities of prokaryotes and fungi throughout the whole composting process of source-separated household wastes, i.e. from the starting material to final mature compost. Peters *et al.* (2000) had characterised several prokaryotes in a composting pile containing shredded maize plants, straw-bedded horse manure and wood chips. *Azotobacter salinestris*, *Bacillus badius*, *Bacillus coagulans*, *Bacillus fusiformis*, *Bacillus smithii*, *Clostridium stercorarium subsp. thermolacticum*, *Geobacillus caldolyticus*, *Lactobacillus confusus*, *Lactobacillus panis*, *Pseudomonas citronellolis*, *Pseudomonas stutzeri*, *Thermobispora bispora*, *Thiobacillus denitrificans* and *Xanthomonas campestris* were identified.

Composting is applied in bioremediation as a means of degrading toxic organic compounds and perhaps lessening the toxicity of metallic contaminants in organic residues, wastes, and by-products (Cai *et al.* 2007a; Dolliver *et al.* 2008; Saviozzi *et al.* 2009; Anastasi *et al.* 2008; O'Donnell *et al.* 2001; Zeng *et al.* 2007; Fountoulakis *et al.* 2010). The processes of bioremediation in composting are similar to those that occur biologically in soil whereby the degradation of organic matter (OM) from organic amendments used in the remediation of metal contaminated soils leads to changes in the soil chemical properties shortly after their addition, and which may affect the soil metal distribution (Clemente *et al.* 2006). Büyüksönmez *et al.* (1999) have performed an extensive review on the fate of pesticides during composting and have concluded that the mechanisms of degradation indicated that mineralization might account for only a small portion of pesticide disappearance. The other prominent fates included partial degradation to secondary compounds, adsorption, humification, and volatilization (Carrillo-González *et al.* 2006). Composting may accelerate the destruction and/or fixation of contaminants (Rao *et al.* 1995, 1996) by virtue of the wide variety of microbes native to the composting environment. Temperatures being generally higher in composts than in soils, result in an increased solubility of contaminants and a higher metabolic activity. Moreover, high levels of substrate in composts can also lead to microbial co-metabolism and the degradation of the organic contaminants such as pesticides (Johnsen *et al.* 2005; Okpokwasili and Nweke 2006) and sequestration of the inorganic pollutants species.

HEAVY METAL METABOLISM IN COMPOSTING ENVIRONMENTS

Unlike organic compounds, HMs cannot be biodegraded to simple and less harmful, if not harmless molecules. Hence, the clean-up of HMs pollution requires the immobilization and toxicity reduction or complete removal of the HMs ions. In recent years, scientists and engineers have started to generate cost effective technologies which include the use of microorganisms/biomass or live plants for cleaning of polluted areas (Kuzovkina *et al.* 2004). The fate of toxic metallic cations in contaminated soil environments depends largely on the interactions of these metal ions with the inorganic and organic surfaces. The extent to which a metallic cation interacts with these surfaces determines the concentration of metal in solution and, consequently, the potential

for movement into groundwater or uptake by plants or biomass (Marques *et al.* 2009). In so happening, the HMs ions are immobilized, sequestered and rendered biochemically safer. The application of the composting process for the remediation of HMs and HM-contaminated media such as soils and wastewaters is a relatively recent technique used in environmental clean-up (Gao *et al.* 2007). The findings of Paré *et al.* (1999) also support that co-composting HM contaminated residues can substantially reduce the extractability and exchangeability of HM like Zn, Cr, Cu and Pb, thereby reducing the risks of these entering the food chain and contaminating crops, animals and water reserves.

Metal speciation information during the composting process can provide useful insight into the metal-microbial interaction and would help in the evaluation of the quality of composts. This would thence facilitate the exploitation of composts in the remediation of heavy metal contaminated land. Greenway and Song (2002) employed a systematic approach to metal speciation in compost by applying a three-step method for operationally defined metal speciation of soils and sediments, developed by the European Commission's Standards, Measurement and Testing Programme to monitor the change in metal speciation with time for four different waste composting processes. Their results have shown that in general metals become less available for the first extraction step as the composting process proceeds, and this would in principle imply that composting tends to redistribute the heavy metals from more labile forms to more fixed forms. This mechanism may then explain why the application of composts could be useful for with heavy metal contaminated land.

Different physical, chemical and biochemical processes take place during the remediation of the HMs during composting but the detailed and successive pathways taking place during composting and their effects on HM content are largely unknown (Bhattacharyya *et al.* 2004). Nevertheless, the first major group can be grouped into physico-chemical processes that promote and regulate mechanisms such as solubility and precipitation, adsorption, complexation, and occlusion/encapsulation (Carrillo-González *et al.* 2006). The processes that sequester HMs can be grossly termed sorption which, to a large extent, determines the partitioning between the solid and solution phase. These processes can be expected to predominate in severely metal-contaminated soils as biological processes could be limited by the toxicity of the metals of concern (Carrillo-González *et al.* 2006).

Complexation of HMs takes place in most cases with a significant proportion of the soluble metals occurring in association with dissolved organic matter (DOM) of the composts (Carrillo-González *et al.* 2006). This DOM is composed of a heterogeneous mixture of fulvic and humic acids (humic substances (HSs)). HSs are breakdown products of plants and biological origins found in almost all terrestrial and aquatic environments that cannot be exactly classified as any other chemical class of compounds (e.g., polysaccharides, proteins, lignin). The size, molecular weight, elemental compositions, structure, and the number and position of functional groups of HSs vary depending on their origin, method of extraction, and natural condition prevailing their formation. HSs are operationally be classified as three fractions according to their solubility in water: fulvic acid (FA), humic acid (HA) and humin. FAs are those organic materials that are soluble in water at all pH values. HA are those materials that are soluble only above pH 2. Humin is the fraction of natural organic materials that is insoluble in water at all pH. Although precise structure of HA and FA is not attainable, the knowledge of the basic structure is required for a full understanding of the properties and function of these constituents in the environment. The main advantages of hypothetical models are:

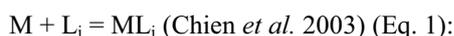
- (1) as a means of representing the average properties of HA and FA,
- (2) to help in the formulation of new hypotheses regarding their structures and the development of innovative ex-

perimental schemes for the investigation, and
(3) for illustrating mechanisms of the binding of metal ions and organic compounds.

Humic and fulvic substances have a high capacity to interact with metal ions and organic and mineral substances, forming soluble or non soluble complexes with varied stability and physico-chemical properties. The involved processes are: mineral dissolution, formation of metal complexes soluble in water, formation of metal-ligand complexes soluble in water, adsorption/desorption processes (solid phase) of metallic ions, adsorption onto external mineral surfaces and adsorption onto inter-laminar mineral surfaces (Benedetti and Van Rinniburgh 1995). Given that these natural ligands occur at rather large concentrations in composts (Laborda *et al.* 2008; Hachicha *et al.* 2009) and have variable chemical composition and structure, complexation with natural organic acids from composts becomes difficult to model. Complexation can be subdivided among weakly bound ion pairs, complexes and strong ligands (Carrillo-González *et al.* 2006). Ion pairs refer to electrostatic interactions of a metal with an inorganic anion where the hydration shells of the ions are largely unaffected. In complexation, part of the bonding is covalent and the hydration shells of the ions are reduced, whereas with chelate ligands metals usually have more than a single binding site (Dudev and Lim 2008) and with little of the hydration shell retained.

In soil and the associated environments, naturally occurring humic substances exert strong binding strength with metals (including heavy metals). It is generally attributable to the interaction of metal ions with two important acidic binding sites of carboxylic and phenolic hydroxyl groups of humic substances (Vinkler *et al.* 1976; Piccolo and Stevenson 1981). Organic ligands derived from humic substances react with heavy metals to form complexes, which influence the concentrations of free and labile heavy metal ions and their subsequent mobilities and biotoxicities in soil and the associated environments (Gregor and Powell 1988).

According to the equilibrium description of metal complexation elucidated by Perdue (1985), the reaction between a metal ion (M) and a single binding site (Li) to form a 1:1 complex can be described by a formation constant, as exemplified by the formation constant for the reaction:



$$K_i = \{ML_i\} / \{M\} \{L_i\} = [ML_i] / [M][L_i] \cdot \gamma_{ML_i} / \gamma_M \gamma_{L_i} = K_i^c \Gamma_i$$

where M is a metal aquo ion, L_i is a fully deprotonated binding site, ML_i is the complex formed from one mole each of M and L_i , braces { } and square brackets [] denote activities and concentrations, respectively, and γ -values are activity coefficients. The formation constant K_i is a true thermodynamic constant, independent of solution composition. The concentration quotient K_i^c and the activity coefficient ratio Γ_i are, however, complementary functions of ionic strength (Chien *et al.* 2003). For mathematical convenience, a conditional concentration quotient K_i^* is often defined in which the precise terms in Eq. (1) are replaced by more convenient terms (Eq. 2):

$$K_i^* = [ML_i \text{ (bound)}] / [M \text{ (free)}][L_i \text{ (free)}]$$

In this equation, M (free) represents all forms of the metal ion that are not bound to the ligand of interest, L_i (free) represents all forms of the ligand that are not bound to the metal ion, and ML_i (bound) represents all complexes of 1:1 metal: ligand stoichiometry. Unlike K_i^c , which is only a function of ionic strength, K_i^* is a function of ionic strength, pH, concentrations of competing metal ions and ligands, and so on. If all side reactions are well understood, K_i^* is a useful parameter that can be directly related to K_i^c . The extension of this treatment to a complex mixture such as humic substances is straightforward (Chien *et al.* 2003).

Inasmuch as the individual components of such mixtures are unknown, it is impossible to rigorously describe

the competing side reactions of the ligand mixture. Conditional concentration quotients or related hybrid expressions are thus used exclusively, and an “average” conditional concentration quotient is often defined by formal analogy with Eq. (2) (Chien *et al.* 2003) (Eq. 3):

$$K^* = \frac{\Sigma[ML_i(\text{bound})]}{[M(\text{free})]\Sigma[L_i(\text{free})]}$$

where $\Sigma[ML_i(\text{bound})]$ is the sum of the concentrations of all complexes formed between M and the multiligand mixture, $\Sigma[L_i(\text{free})]$ is the sum of the concentrations of all binding sites that are not associated with M, and M (free) is the sum of all metal species that are not associated with the multi-ligand mixture.

There are also high significant correlations between different forms of HM content and degree of humification for the elements. Ciavatta *et al.* (1993) had reported high correlations between HM content and the degree of humification for Cu, Zn, Pb, Cr, Ni and Cd for composts produced from municipal solid wastes (MSW) both with and without the removal of inert components prior to the beginning of the composting process, and with most of the extractants. The biochemical reactions in the composting process therefore increase the humic acid content as opposed to the fulvic acid and this transformation is mainly responsible in serving as a binding agent for the HMs thereby moderating the rapid metal mobilization (Bhattacharyya *et al.* 2004). The effects of humic acids (HAs) isolated from mature compost on the distribution of HMs and on organic-C mineralisation in two contaminated soils were studied in incubation experiments by Clemente and Bernal (2006). HAs were added to an acid soil (pH 3.4; 966 mg kg⁻¹ Zn and 9,229 mg kg⁻¹ Pb as main contaminants) and to a calcareous soil (pH 7.7; 2,602 mg kg⁻¹ Zn and 1,572 mg kg⁻¹ Pb as main contaminants) at a rate of 1.1 g organic-C added per 100 g soil. Clemente and Bernal (2006) concluded that HA-rich materials like composts could be useful amendments for soil remediation involving stabilization, although a simultaneous but slight mobilization of Zn, Pb and Cu could be provoked in acidic soils.

HMs in composts

HMs composition of composts varies widely depending on the sources, composting process (He *et al.* 1992) and geographical location (Krogmann 1999). The levels of HMs in MSW composts have been reported for many countries in the world by several authors (He *et al.* 1992; Koivula *et al.* 2000). Like soils, sediments and sludge, HMs can exist in a variety of forms in composts. These forms include (i) water-soluble, (ii) exchangeable, (iii) linked to organic substances, (iv) locked or co-precipitated with oxides, carbonates and phosphates, or other secondary minerals and (v) ions in the crystalline lattices of the primary minerals (Petruzzelli 1989; Iwegbue *et al.* 2006a, 2006b). The first three chemical forms are considered to be balanced among themselves and this equilibrium is influenced by pH and the concentrations of metals and ligands. The metals present in these forms are considered to be most available forms of plant nutrition, each successive form representing less availability.

The water-soluble fraction of HMs is the most biologically active form (Iwegbue *et al.* 2007). The high toxicity potential of this fraction is proven by the higher sensitivity exhibited by plants grown in hydroponic media. The water soluble fraction has the highest potential of contamination of food chain, surface water and groundwater (Leita and De Nobili 1991). Leita and De Nobili (1991) reported a progressive increase in total metal concentration during composting as a result of mineralization of organic matter (Barker and Bryson 2002). During composting, the species of HM often change and in turn alter the availability to plants, which would also change metal availability (Simeoni *et al.* 1984; Giordano *et al.* 1975). Amir *et al.* (2005) have reported that the total metal contents in final composts were much lower than the limit values of composts to be used as

good soil fertilizer. Furthermore, it was observed that at different steps of treatment, a large proportion of the HMs were associated to the residual fraction and more resistant fractions to extraction X-NaOH, X-EDTA, X-HNO₃. Less than 2% of metals had been found bound to bioavailable fractions X-(KNO₃ + H₂O). In addition, Amir *et al.* (2005) found significant degrees of correlation between the HM fractions and the changes of pH, ash, organic matter, humic substance during the composting process.

Metallic contaminants may enter composts from farm manures (Sims and Wolf 1994), sewage sludges (Hyun *et al.* 1998), MSWs (Barbarick *et al.* 1998), and pesticides (Moolenaar and Beltrami 1998). Unlike organic contaminants, metallic contaminants in feedstock are not lessened quantitatively during composting (Barker and Bryson 2002). However, the bioavailability of metallic contaminants may be lessened by composting (Chaney and Ryan 1993). HSs and iron oxides in composts can limit the bioavailability of metals as well as organics in composts. Because of the loss of carbon during composting as a result of microbially mediated mineralization, the concentrations of metallic contaminants in solid wastes may be increased. Paré *et al.* (1999) have reported increases in total concentrations of some residual HMs, ranging from 26 to 145% increases after 41 days of composting of biosolids and MSWs. Paré *et al.* (1998, 1999) suggested that the stabilized organic matter formed complexes with metals and restricted their mobility and bioavailability for plant absorption. However, composting may occasionally release contaminating metals from organic combination by the degradation of the organo-metallic complexes, leading to increased bioavailability of metals (Heyes *et al.* 1998). In raw farm manures and in composts, metals such as Cu are associated with the organic fraction (Leita and de Nobili 1991). Hsu and Lo (2000) reported that the leaching of copper, manganese, and zinc from composted hog (*Sus scrofa*) manure was low due to interactions of the metals with the organic material in the compost. Immature composts, however, had a higher potential for leaching of copper than mature composts. Some of this effect may have been pH-related, as extractable manganese and zinc were low in alkaline conditions (Barker and Bryson 2002). On the other hand, in alkaline-stabilized sludges, leaching of metals may be high, due to the dissolution of organic matter at high pH (McBride 1998).

HM-composts interactions

The physical, chemical and biochemical processes during composting which cause the uptake of HMs may occur individually, successively or in competition with each other. These processes and mechanisms determine the fate of HMs during the composting process and/or in response to composts. Garcia *et al.* (1995) had studied the influence of composting on sewage sludges contaminated with high concentrations of Cd, Cu, Ni and Zn. The contamination by Cd led to a much lower degree of nitrification during the composting, and hydrolytic enzyme activities showed that large quantities of HMs could have a negative effect on urease synthesis. Similarly, HM contamination negatively affected phosphatase; although not β-glucosidase, which increased with the level of contamination. Interestingly, the composting process had rendered insoluble that portion of the metals which could be extracted with diethylene triamine pentacetic acid (DTPA), CaCl₂ or H₂O by forming metal-humus complexes. Of the metals which were present at high quantity in the sewage sludges (Ni, Cu, Zn and Cd), Ni was the most easily extracted by H₂O or CaCl₂ and was therefore to be the one most weakly bound to the organic matrix of the composting substrates, while Zn, in contrast, remained strongly bound. Paré *et al.* (1999) have determined the chemical distributions of Cu, Zn, Cr, Pb, Ni and Co by eight sequential extractions of co-composted materials sampled during an entire composting period. It had been found that the concentrations of residual Zn, Cr, Cu and Pb had increased by 145, 124, 73.6 and 26.3% whereas

the concentration of residual Ni remained relatively constant while that Co decreased by 60% over the same period. From a mechanistic point of view, the Fourier–transform infrared (FTIR) spectra indicated that the HMs in the compost had bonded to the COO– groups of the organic matter.

Grimes *et al.* (1999) reported that the relative binding of Cd, Cu, Pb, and Zn contained in natural compost was in the order $Pb > Cd \approx Cu > Zn$, with the sorption of metals on compost taking place, at least in part, by the exchange of calcium bound to the compost in both humic and non-humic sites in the compost. Gibert *et al.* (2005) have evaluated the potential of a mixture of municipal compost and calcite in an upflow packed column to promote sulphidogenesis in the remediation of a simulated mine water containing HMs. Their results showed that Fe, Al, Zn and Cu were significantly removed, and the removal was attributable to the combined precipitation as metal (oxy)hydroxides and carbonates, co-precipitation with these (oxy)hydroxides and sorption onto the compost surface rather than to precipitation as metal sulphides. The two last mechanisms had been determined to be especially significant for Zn, whose hydroxide was not expected to precipitate at pH 6–7. Gibert *et al.* (2005) proposed that before the saturation of compost sorption sites, 60% of the influent Zn had been removed by co-precipitation with Fe– and Al–(oxy)hydroxide and 40% by sorption onto the municipal compost. Malley *et al.* (2006) have investigated the effect of Cu and Zn on dehydrogenase and protease activity of the substrate during vermicomposting on their bioaccumulation and impact on the reproduction of *Eisenia fetida*. It was found that the Cu ions had accumulated within the worm tissues in dosage concentrations up to a maximum level of 213 mg Cu kg⁻¹ and the number of juveniles decreased from the lowest to highest dosages of Cu and Zn after 10 weeks of the experiment. It was also determined that dehydrogenase showed a strong negative correlation with increased dosage of Cu, while protease remained unaffected. Hence, reductions in dehydrogenase activity with increasing dosages of Cu and Zn indicated that these metals would most probably impact detrimentally on the microbiology and consequently the stabilization of the dosed media, and affect the biodegradation rates of bioavailable organic matter in the composting matrices.

HM distribution and bioavailability also show some changes during composting depending on the metal itself and the physico-chemical properties of the medium (Amir *et al.* 2005). Bioavailable fractions of all elements tend to decrease except Ni–H₂O. Zn and mainly Cu present more affinity to organic and carbonate fractions. In contrast, Pb is usually preferentially bound to sulphide forms X–HNO₃ while nickel shows a significant decrease of organic form. Cai *et al.* (2007b) have monitored the concentrations and speciation of HMs in six different composts of sewage sludges deriving from two wastewater treatment plants. Cai *et al.* (2007b) found that in all the final composts, more than 70% of total Cu was associated with the organic matter-bound fraction, while Zn was mainly concentrated in the exchangeable and Fe–Mn oxide-bound fractions which implied the high mobility and bioavailability. In a study on the treatment of sewage sludge by forced-aeration composting, Zheng *et al.* (2007) found that the Ni and Cr concentrations had increased by 30.4 and 36.0%, respectively. All the more, exchangeable, carbonate-bound, Fe–Mn oxide-bound, and organic matter-bound Ni and Cr were transformed to residual fractions. For Cr, the carbonate-bound, Fe–Mn oxide-bound, and organic matter-bound fractions were major contributors, while organic matter-bound Ni was a major contributor to the residual fraction.

Speciation of HMs in composting media and composts

The effect of HMs in composts on crops and the receiving bodies can only be attained from precise knowledge of the HM speciation and the response to plant species (Iwegbue

et al. 2007). In addition, speciations will determine HM mobility and hence their potential contamination of groundwater following compost application. The methods used to characterize HMs in solid phase of composts and compost amended soils include physical fractionation and chemical extraction. Chemical extraction schemes are the most frequently used approach to fractionate trace metals in soils, sewage sludge and composts, and several variations exist in the sequential extraction procedures (Iwegbue *et al.* 2007). These variations include reagent types, strength, volume and extraction time. However, a major drawback shared by all sequential extraction schemes is the complexity and time consuming nature of the procedures (Liu *et al.* 2007). Garcia *et al.* (1990) studied the simplest sequential chemical extraction technique with CaCl₂ and DTPA to examine the extractability of metals over composting time. It was reported that CaCl₂ extractable Fe, Cu, Mn, Zn, Ni and Pb as percentage of total metal content decreased after 90 days of composting. DTPA extractable Fe, Mn, Ni and Pb decreased but DTPA extractable Cu and Zn increased from 14 to 18% and 27.1 to 35.2%, respectively. DTPA hence always extracted considerably more trace metals than CaCl₂ except for Fe, in which CaCl₂ extracted more Fe than DTPA. This suggested that the organic compounds had bound more trace metals than held on the exchange sites. Fractionation techniques using different reagents (salts, bases and in some cases, acids) are used to assess how elements change their chemical state in response to changing soil conditions, and to identify the chemical species present in the solid phase (Chang *et al.* 1994).

Compost application and HMs transformations

The major technical concern with land application of sewage sludge composts is the high concentrations of HMs. These HMs may leach and enter the ecosystem, the food chain, and eventually the human population (Liu *et al.* 2007). Hence, the need to assess the limitations of compost use on agricultural soils has created a demand for information on the availability of metals in municipal solid waste and sewage sludge composts (Leita and De Nobili 1991). The degree of stabilization reached by organic matter appears to be an important factor in determining the potential mobility and uptake by plants of the HMs.

Chiu *et al.* (2006) have conducted a greenhouse study to evaluate the feasibility of using *Vetiveria zizanioides* (vetiver) and *Phragmites australis* (common reed) for the reclamation of Pb/Zn and Cu mine tailings and to assess the effects of using manure compost and sewage sludge as organic amendments on the revegetation of these tailings. Results revealed that the applications of manure compost or sewage sludge not only increased N, P and K concentrations, but also decreased DTPA extractable Pb and Zn contents in Pb/Zn tailings and DTPA-extractable Cu contents in Cu tailings. Plant tissue analysis also showed that the application of manure compost and sewage sludge had significantly reduced the Pb uptake and accumulation, but not Cu in both vetiver and common reed. Topcuoğlu (2005) also observed an increase in both total and DTPA-extractable concentrations of Zn, Cu, Ni and Pb in a two-year study where manure, sewage sludge and MSW compost were applied to greenhouse soil with tomato plants being grown. Topcuoğlu (2005) also reported that the amount of bioavailable metals in the greenhouse soil were significantly higher for the sewage sludge and MSW compost treatments, almost including a 9-, 6- and 3-fold increase in Zn, Cu and Pb, respectively. Oleszczuk (2008) have observed that the composting process significantly influenced on Ni, Cd, Cr and Pb content in a very few number of cases. An increase of HMs content was noted in the case of Cd, Cr and Ni whereas Pb content decreased. Oleszczuk (2008) explained this rare increase in the sewage sludge toxicity after their composting to be the result of the formation of toxic metabolites of organic compounds, or condensation of HMs as a result of mass losses taking place during the compos-

ting process. Usman *et al.* (2004) explained that observed increase of mobile Zn, Cd, Cu, and Ni in soil amended with sewage sludge as a result of a high content of heavy metals in sewage sludge, the formation of soluble HMs–organic associations and a decrease in soil pH. Liu *et al.* (2007) found that the residue fraction for Pb, Zn and Cd had decreased but those for Ni and Cr had increased and with the Cu residue fraction being quasi constant. Also, the contents of the total mobile fractions for Zn and Pb were significantly increased, and there were significant degrees of correlation between HM fractions and changes of pH, composting temperature, and OM content.

Bartl *et al.* (2002) investigated the influence of different fertilization systems (consisting of biowaste compost and mineral fertilizer) on the nutrient and HM contents of soil and plants. Bartl *et al.* (2002) reported that the five-year fertilization with composted biowaste did not influence the total contents of Cd, Mn, Mo, and Ni in soil, but the total soil contents of Zn and Pb were significantly higher in soils of the BC treatment than in the unfertilized control, while the mineral fertilization had inhibited the Mo uptake by plants. The effects of two differing organic amendments on OM mineralization and fractionation of HMs in a contaminated soil have been investigated in an incubation experiment by Clemente *et al.* (2006). Treatments were done with a control unamended soil, soil amended with fresh cow manure, and soil amended with a compost having a high maturity. It was reported that both amendments had favoured Zn and Pb fixation, particularly the manure, while Mn solubility increased at the beginning of the experiment due to a pH effect, and only Cu solubility increased through organic matter chelation in both amended soils.

Zhang *et al.* (2004) have evaluated the solubility and fractionation of heavy metals in media containing 0, 25, 50, 75, or 100% compost derived from biosolids and yard trimmings for potential impacts on the environment. As compost proportion in peat-based media increased from 0 to 100%, concentrations of Cd, Cu, Ni, Pb, Zn, and Mn in the media increased whereas concentrations of total Co and Cr decreased. Except for Cu, all HMs in the water-soluble fraction decreased with increasing compost proportion in the media, because of higher Fe, Al, and Ca concentrations and pH values of the composts than the peat. When the media pH was controlled and maintained at normal range of plant growth (5.5–6.5), leaching of the HMs was found to be minimal. For all elements, the amounts extracted depended highly on pH, and water solubility of all elements increased sharply with decreasing pH. The pH values at which a sharp increase in element concentration occurred were 4 to 5 for Cd, Cu, Co, Cr, Ni, Zn, and Pb. At pH 5.0 to 8.0, solubilities of heavy metals, including Cd, Co, Cr, Pb, Zn, and Ni, were generally low, and the released percentages of Cd, Co, Cr, Cu, Ni, Pb, and Zn at pH 5 to 8 were 3.2, 1.4, 0.3, 2.9, 2.8, 1.4, and 2.5%, respectively. A possible explanation could have been that adsorption of the metal ions on hydrous oxide of Fe or Al, or coprecipitation with CaCO_3 at this pH range, was high. The pH values of media amended with varying rates of compost ranged from 6.52 to 6.86, thus falling within this pH range. Media amended with compost have a relatively high pH value and, thus, minimize environmental pollution by soluble heavy metals. However, when pH was greater than 8.0, the solubility of Cu increased sharply, probably because of an increase in dissolution of organic complex Cu at high pH. The variation in the solubilities of heavy metals at different pH values was larger than the variation due to a difference in compost proportion. Thus, pH seems to be the dominating factor controlling water solubility of the metals.

The concentrations of heavy metals in the media recovered by five successive water extractions were also used to assess the leaching potential of these elements. Leaching potential of the elements varied with compost rates and water extraction sequence. In the first extraction, soluble Cd, Co, Ni, Pb, Zn, and Mn decreased (52.3 to 3.1 $\mu\text{g kg}^{-1}$ for Cd, 36.5 to 21.0 $\mu\text{g kg}^{-1}$ for Co, 518.8 to 306.5 $\mu\text{g kg}^{-1}$ for

Ni, 417.7 to 83.4 $\mu\text{g kg}^{-1}$ for Pb, 4.75 to 1.08 mg kg^{-1} for Zn, and 6.98 to 0.68 mg kg^{-1} for Mn), whereas Cr, Cu, and P increased (17.4 to 41.5 $\mu\text{g kg}^{-1}$ for Cr, 0.68 to 1.86 mg kg^{-1} for Cu, and 189.7 to 241.8 mg kg^{-1} for P) with increasing compost.

Furthermore, the metal accumulation and DTPA-extractability in a sandy soil of Spain after three successive applications of MSW compost (MSWC) under intensive farming conditions were studied by Madrid *et al.* (2007). MSWC was applied for three consecutive crops in a plot of the soil in a greenhouse at a rate of 2.1, 2.1, and 1.8 kg m^{-1} on a dry matter basis, respectively. One more crop was planted, but no compost was applied to monitor residual effects of the treatment. A control plot did not receive any compost during the experiment. A rotation of crops was used during the experiment with tomato (*Lycopersicon esculentum*) as the first crop, followed by zucchini (*Cucurbita pepo* var. *melo pepo*), green pepper (*Capsicum annuum*), and finally tomato again. Although moderate rates of MSWC were used and metal content of the compost was below the legal limits in Spain, increases in metal contents were observed in the soil, compared with the control treatment without the MSWC. After the second application of compost, increases in aqua regia-extractable (pseudo-total content) Zn and Pb were found in the 0–25 cm layer, and after the third application, Cu and Ni contents were also increased. Furthermore, increases in DTPA-extractable (available content) concentrations of metal contents were observed at higher rates than in aqua regia extractable contents, suggesting that metals added with compost were more available than native metals in soils. Madrid *et al.* (2007) concluded that the increases in the available fraction of the metal after MSWC application, the sandy characteristics of the soil, and the high irrigation rates practiced could have favoured the leaching of the metals through the soil profile. Lately, O'Dell *et al.* (2007) have conducted a battery of laboratory and greenhouse studies to better understand how Cu and Zn toxicity influences *Bromus carinatus* (Hook and Arn.) growth and to what degree a yard waste compost amendment could reduce Cu and Zn bioavailability in Cu–Zn minespoil and promote plant growth in combination with fertilizer. It was reported that the compost amendment had exceptionally high Cu and Zn binding capacities at 0.17 and 0.08 $\text{g metal g}^{-1} \text{C}$, for Cu and Zn, respectively. Further analysis showed that these high binding capacities were due to high compost humic and fulvic acid concentrations and that the compost amendment had decreased the toxic bioavailable HM concentrations in the metalliferous minespoil.

Plant roots can play an important role in the transformation and chemical speciation of HMs in soils and composts (Yang *et al.* 2005). Three mechanisms can be influenced by plant roots: modification of the compost environment in the rhizosphere, transformation of chemical form of HMs, and biosorption (Carrillo–González *et al.* 2006). Roots exude plant metabolites including several forms of carbohydrates and organic acids that can serve as energy source for compost microbes. These low molecular-weight organic acids can complex metal ions rendering them potentially more mobile and bioavailable. Microbes can also carry out important biotic redox reactions for some HMs (Mahimairaja *et al.* 2005) including the transformations of multivalent anionic HMs, such as As, Cr, and Se by altering their oxidation state and chemical species. A number of studies (Hussein *et al.* 2005; Şahin and Öztürk 2005; Lu *et al.* 2006; Wang and Chen 2006; Chen and Wang 2007; Romera *et al.* 2007; Sheng *et al.* 2008; Choi *et al.* 2009; Choudhary and Sar 2009; Ertuğrul *et al.* 2009; Vala 2010) have reported the use of biotic species such as bacteria, fungi and algae in being successful in uptaking HMs.

HMs sorption on composts

Metal adsorption to soil after the application of organic wastes has been studied in single metal systems (Zhou and Wong 2001). On the other hand, few studies have investi-

gated the competitive metal adsorption in terms of the quality of organic matter in soils amended with sewage sludge, composted sewage sludge or other composts. Research efforts have in preference been focused on the evaluation of HM mobility, partitioning and sorption in temperate soils (Walter *et al.* 2002).

The interaction of Cu with dissolved organic matter (DOM) is an important physicochemical process affecting Cu mobility in soils. The aim of the study of Zhou and Wong (2001) was to investigate the effects of DOM from anaerobically digested dewatered sludge and sludge compost on the sorption of Cu on an acidic sandy loam and a calcareous clay loam. The results of this specific study have been of particularly high significance in elucidating part of the metal-DOM interactions. The amount of Cu sorbed increased with an increase in equilibrium Cu concentrations and eventually attained a plateau value at high equilibrium Cu concentrations. The sorption capacity of the calcareous soil for Cu was much higher than that of the acidic sandy loam at the same equilibrium concentration of Cu, which might be because of the higher pH, clay mineral and carbonate contents, and higher CEC of the calcareous soil. More variable negative charges and sorption sites were formed in the soil of higher pH and clay mineral contents, which favor Cu sorption.

On the other hand, the higher pH and carbonate contents may also facilitate Cu precipitation as $\text{Cu}(\text{OH})_2$ and/or CaCO_3 . In the presence of DOM, the Cu sorption capacity decreased markedly for both soils, but the effect on the calcareous soil was greater than that on the acidic sandy loam. Dissolved organic matter derived from sludge compost had a smaller effect in reducing the sorption capacity for Cu than that of sludge for both soil types. The origin and concentration of DOM affected not only the Cu sorption of the two soils, but the desorption of Cu sorbed previously in the sorption study. A relatively higher desorption was found for Cu sorbed in the presence of a higher concentration of DOM, especially for sludge DOM treatment. This might result from a stronger binding affinity of Cu with sludge DOM, and as a result it hinders partly the precipitation of Cu as $\text{Cu}(\text{OH})_2$ under such a high-pH condition, as compared with compost DOM. In addition, it was assumed that the higher affinity of the Cu-compost DOM to the soil matrix may also contribute to this phenomenon. This implied that Cu mobility might be facilitated greatly in the soil receiving DOM, especially for sludge DOM, because of the reduction of Cu sorption onto soil and the relatively ready desorption of Cu sorbed previously in the presence of DOM. The differences in Cu sorption and desorption behavior caused by DOM of different original materials appeared to be closely related to the chemical components of DOM. Sludge compost DOM contained a relatively greater amount of high molecular weight hydrophobic fractions, especially hydrophobic acid (HoA) and hydrophobic neutral (HoN), but fewer hydrophilic fractions, especially hydrophilic base (HiB) and hydrophilic acid (HiA), than that of sludge DOM.

The Fourier transform infrared (FT-IR) spectrum from Zhou *et al.* (2000) showed that the hydrophobic fraction had a considerably more aromatic acids or aromatic phenols, while the hydrophilic fraction was richer in carboxyl and polyhydroxyl groups. Sludge DOM appeared to have more C-N and C-O groups of a chelating feature, possibly from organic acid, amino acid, and amines, than compost DOM, especially for the HiA, HiB, and HoA fractions. Keefer *et al.* (1984) pointed out that the HiB fraction was mainly comprised of N-containing groups including most amino acids, amino sugars, low molecular weight amines, and pyridine, while the HiA fraction contained the components of the -COO functional group, such as uronic acids, simple organic acids, and polyfunctional acids, which resulted in the higher affinity of Cu with HiB. In addition, many researchers also revealed that hydrophobic fractions of DOM bind more strongly on soils and minerals than the hydrophilic fractions (Jardine *et al.* 1989; Gu *et al.* 1995; Kaiser *et al.* 1997). Liang *et al.* (1996) found that increased sorption of the

DOM extracted from the composted manure is probably due to an increase in molecular weight of the major DOM components. It is reasonable to presume that the reduction of mobile DOM in the soil receiving sludge compost DOM was due either to sorption of greater amounts of compost DOM in comparison with sludge DOM by the soils, or the formation of a Cu-compost DOM complex. The Cu-compost DOM complex could be sorbed repeatedly by the soils, although DOM sorption by soils was not measured in this study. In contrast, sludge DOM contained more HiB fraction, which was not readily sorbed by soils but could strongly associate with Cu. Thus, sludge DOM had a stronger capability to reduce Cu sorption by soils than did compost DOM.

The agricultural practice of amending soils with composted municipal solid waste (MSW) adds significant amounts of organic matter and trace metals, including Cd. Under these conditions, soluble organic complexes of Cd formed in the compost may be more significant than previously thought, due to Cd bioavailability and mobility in the soil environment. To study the relative importance of different types of organic ligands in MSW compost for the binding of Cd, six fractions of the DOM in addition to humic acid (HA) and fulvic acid (FA) were extracted and their complexation of Cd quantified at pH 7 using an ion-selective electrode (ISE) in an elaborate study by Kaschl *et al.* (2002). The highest complexing capacities (CC) for Cd were found for the most humified ligands: HA (2,386 $\mu\text{mol Cd g}^{-1} \text{ C}$ of ligand), predialyzed FA (2,468 $\mu\text{mol Cd g}^{-1} \text{ C}$), and HoA, a fulvic-type, easily soluble fraction (1042 $\mu\text{mol Cd g}^{-1} \text{ C}$). The differences in CC for Cd of the various organic ligands were not directly related to total acid-titratable or carboxylic groups, indicating the importance of sterical issues and other functional groups.

A fairly good third-degree polynomial fit could be achieved for data of HA, FA > 1000, HoA, HiN, and HiA. Data points for FA, HoN, and HiB from different titrations were somewhat divergent, possibly because of the more heterogeneous nature of these fractions. The strongest binding sites (pK_{int}) for Cd at low ratios of Cd to ligand were found on HA (pK_{int} 10.05), followed by HiB (pK_{int} 8.11). The pK_{int} for all other fractions was similar: 7.98 for FA 1000, 6.80 for FA (here the polynomial fit was not satisfactory, hence pK_{int} values for the continuous model were not calculated), 7.74 for HoA, 7.69 for HoN, 7.02 for HiA, and 6.93 for HiN. These stability constants are high in comparison with literature data obtained for humic substances. This may be due to the relatively high pH (7) and the low ionic strength (0.01 M) of the tested solution. Both factors have indeed been reported to result in higher formation constants (Saar and Weber 1979; Stevenson *et al.* 1993; Logan *et al.* 1997). It has also been recognized that association constants for metal-organic complexes in the literature are often unrealistically low, since they are based on measurements at high metal loadings on the complexing sites of OM (McBride *et al.* 1999). The metal binding at the strongest binding site at low metal to ligand ratios is not monitored well by the discrete (noncontinuous) models due to a limitation of the method sensitivity. Trace metals, in fact, occupy different and more selective bonding sites at low metal levels (McBride *et al.* 1999).

At present, there are only a few studies regarding the treatment of wastewaters containing HMs by vermicompost. However, Jordão *et al.* (2002), Carrasquero Durán *et al.* (2006), Jadia and Fulekar (2008), Urdaneta *et al.* (2008) and Jordão *et al.* (2009) have found that metal concentrations in the purified effluents were below the maximum values established for waste discharges by the prevalent local standards. They also reported that the vermicompost residues obtained from the metal retention process could be applied as a fertilizer to agricultural lands. Vermicompost is a 'peat-like' material with high porosity, aeration, drainage, water holding capacity and microbial activity (Ansari 2008; Sharma *et al.* 2009; Munnoli *et al.* 2010). It contains most nutrients in plant available forms such as nitrates, phos-

phates, exchangeable calcium and soluble potassium and has large particular surface area that provides many microsites for microbial activity and for the strong retention of nutrients (Singh *et al.* 2008). Humic materials extracted from vermicomposts have been reported to produce auxin-like cell growth and nitrate metabolism of carrots. However humic substances can occur naturally in mature animal manure, sewage sludge or paper-mill sludge but their amount and rates of production are increased dramatically by vermicomposting (Romero *et al.* 2007). Vermicompost has been proposed as a biosorbent for removing metallic ions such as Pb, Ni, Cr and V from wastewaters by Urdaneta *et al.* (2008). They reported it as a promising alternative for decontamination taking advantage of the humic and fulvic substances interaction with metals. The following discussion focuses on the research advances that have been realized when using composts for the removal of some HMs by adsorption onto compost as biosorbent.

Jordão *et al.* (2002) reported that Cu, Zn and Ni retention by cattle manure vermicompost from electroplating wastes were close to 100%. They also reported that it was not necessary to correct the effluent pH during the treatment process to reach the levels recommended by Brazilian legislation for discharge into water courses. Ulmanu *et al.* (2003) and Chen *et al.* (2005) have investigated the sorption of Cd ions onto two other types of composts. Ulmanu *et al.* (2003) found that of all the adsorbents studied, bentonite and compost presented the highest removal efficiencies, reaching 99% for copper when cadmium is also present while Chen *et al.* (2005) found that the maximum uptake estimated with the Langmuir isotherm model were 833.33 mg g⁻¹ for Cd²⁺, 1,000.00 mg g⁻¹ for Pb²⁺ and 44.44 mg g⁻¹ for Cr³⁺, respectively, when spent mushroom compost of *Lentinus edodes* was used as a biosorbent for adsorbing cadmium, lead and chromium from solutions under batch conditions. All the results showed that vast potential sorption capacity was existed in the biomass (compost) for adsorbing these three kinds of metals studied. Carrasquero Durán *et al.* (2006) have studied the adsorption of Pb²⁺ on vermicompost at 11, 30 and 50°C by using Langmuir and Freundlich models. The maximum adsorption capacities were 116.3; 113.6 and 123.5 µg g⁻¹ for each temperature, respectively. The differences in Fourier Transform Infrared Spectroscopy spectra of vermicompost at pH 7.0 in the region from 1,800 to 1,300 cm⁻¹ were interpreted on the basis of carboxyl acid ionization that reduced band intensity around 1,725 cm⁻¹ producing signals at 1,550 cm⁻¹ and 1,390 cm⁻¹ of carboxylate groups. Lately, a couple of fresh studies on the use of composts for heavy metals adsorption have been reported by Kocasoy and Güvener (2009). Kocasoy and Güvener (2009) determined the retention capacity of compost for copper, zinc, nickel and chromium. For this purpose, experiments in batch-mixing reactors with initial metal concentrations ranging from 100 to 1,000 mg L⁻¹ were carried out. Kocasoy and Güvener (2009) observed that compost could repeatedly be used in metal sorption processes, and their experiments indicated that compost has high retention capacities for copper, zinc and nickel, but not for chromium. Thus, compost is a very good potential biosorbent for copper, zinc and nickel and may find place in industrial applications.

Compost microorganisms and invertebrates can also promote the immobilization of metal ions by biological accumulation. Such accumulation is facilitated by biosorption by the microbial biomass and its byproducts and physiological uptake by organisms through metabolically active and passive processes (Mahimairaja *et al.* 2005). Microbes can dissolve minerals by direct or indirect action under the aerobic conditions prevailing in composting matrices (Kurek 2002). Metals can also be mobilized from minerals by complexation with biomolecules of microbial metabolites. Microorganisms have developed two major strategies of internal sequestration of HMs though the formation of inclusion bodies for instance in vacuoles (Davies *et al.* 1991; Korotaev *et al.* 1992; Haag-Kerwer *et al.* 1999; Davis *et al.*

2003; Yang *et al.* 2005; Shao and Sun 2007; Zhang *et al.* 2008; Kazy *et al.* 2009) and binding of metals to heat-stable proteins, such as phytochelatins and metallothioneins, and stable molecules such as ferrihydrite (Hall 2005). The ability of a microorganism to tolerate and to resist HM toxicity may be summarized as involving more than one of the following mechanisms (Giasson *et al.* 2008): fungal gene expression, extracellular metal sequestration and precipitation, production of metallothioneins (metal binding proteins, avoidance of metals (reduced uptake or increased efflux, formation of complexes outside cells, release of organic acids), intracellular chelation (synthesis of ligands such as polyphosphates and metallothioneins), compartmentalization within leaf vacuoles, loss of leaf during dry or cold seasons, phosphorus plant status or interaction between P and metals (increased P uptake by host plant), biological sorption via glomalin and volatilization. Perales-Vela *et al.* (2006) present a rich and comprehensive discussion the on detoxification of HMs in eukaryotic microalgae by addressing aspects on enzymatically synthesized short-chain polypeptides named phytochelatins (class III metallothioneins), class II metallothioneins (identified in cyanobacteria, algae and higher plants), and class I metallothioneins found in most vertebrates, class III metallothionein biosynthesis and regulation, HM sequestration and compartmentalization to the vacuole through HM-MtIII complexation, a general scheme of HM detoxification mechanism mediated by MtIII in microalgae, HM sequestration to the chloroplast and mitochondria, algae-based biotechnologies for HM remediation.

CONCLUDING REMARKS

In this review, composts and the composting environment have been portrayed as heterogeneous mixtures of biotic (i.e., organic matter, microbes and microbial metabolites) and abiotic (i.e., salts, precipitates and miscellaneous inorganic) materials. In this review, it has also been shown with several examples of relevant studies that phase associations of HMs include water soluble, exchangeable, precipitated, co-precipitated in metal oxides, adsorbed/desorbed or complexed by organic ligands and residual fractions, biosorbed onto composts, and bioaccumulated by various bacterial, fungal and algal species by volatilization, vacuolar compartmentalization, intracellular and extracellular chelation. The phase associations and solubility of the HMs change over composting time and when exposed to composts, thereby altering their bioavailability and mobility.

In summary, an understanding of the various physical and biogeochemical processes and how they are influenced in their individual or competitive effects by certain factors such as pH, temperature, OM content is necessary to predict the fate of HMs in compost-enriched media. Advances in research on HM mobility in such media have become important by reason of the efforts to blend the conventional saturated flow and transport models with more precise biogeochemical models with a view to better simulate and capture the interactive and complex processes in such heterogeneous systems. Nevertheless, the broad conclusion is that composting degrades or binds HM pollutants to innocuous levels or into innocuous compounds and has substantial potential for remediation of such polluted materials.

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