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Review Paper

Bioavailability and Leachability of Heavy Metals during Composting – A Review

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Abstract

Composting is the best-known processes for biological stabilization of sewage sludge, municipal solid waste and other biodegradable wastes. Prepared compost can be used as a soil conditioner in agricultural applications. However, the presence of non-biodegradable and high level of toxic heavy metals in the compost frequently hinders agricultural land application. Uptake of heavy metals by plants and subsequent accumulation along the food chain is a potential threat to animal and human health. The availability of metals in soil depends on the nature of the chemical association between a metal with the organic residual and soil matrix, the pH value of the soil, the concentration of the element in the compost and the soil, and the ability of the plant to regulate the uptake of a particular element. The water soluble fraction is positively the most biologically active and highest potential for contamination of food chain, surface water and ground water. The diethylene triamine penta acetic acid (DTPA)-extractable fraction of metals might represent a supplemental approach to check the bioavailability of heavy metals in the soil and sludge amended soil for plant uptake. The phase association and solubility of metals changes with composting time thereby altering metal availability. The toxicity characteristic leaching procedure (TCLP) is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. If an analysis of any one of the liquid fractions of the TCLP extract indicates that regulated heavy metals are present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for those metals, then the waste is hazardous. Therefore this review examines the water solubility, DTPA extractability and leachability of heavy metals in the compost, which has to be applied to the agricultural field.

Keywords: Composting, heavy metals, bioavailability, leachability.

Introduction

Composting of degradable wastes is seen as a method of diverting organic waste materials from landfills while creating a product, at relatively cost effective that is appropriate for agricultural purposes[1,2]. In addition to the potential beneficial components, some waste materials may also contain non-essential elements, persistent organic compounds and microorganisms that may be harmful to the plants[1]. The presence of heavy metals in composts raises serious concern about the adverse environmental impact as a result of excessive compost application to agricultural lands. High and excessive accumulation of heavy metals in the soil may eventually contaminate both human and animal food chain[1]. Heavy metals can affect the growth, morphology and metabolism of soil microorganisms, and reduce both the size and activity of microbial pools, consequently fertility of the soil reduced[3]. Heavy metals uptake by plants and successive accumulation in human tissues and biomagnifications through the food chain causes both human health and environment concerns[4,5]. Because of this, many countries in the world have established specific guidelines and standards for application of composts in agricultural lands[1]. The guidelines, which are generally based on phytotoxic effects and limited to plant uptake studies normally, specify the maximum allowable total metal concentration and exhibit considerable variation[1].

The increase in heavy metal content in the final compost may be explained by: i. losses of organic carbon, especially as CO_2, during stabilization (mineralization of the organic matter), and ii. the fact that some of the heavy metals which at the beginning of the composting process were not contained in the organic fraction could have become incorporated in the organic fraction by the end of the composting process[6]. The determination of total heavy metals concentration does not provide useful information about risk of bioavailability, toxicity, capacity for remobilization of heavy metals in the environment and chemical forms of a metal in which they are accessible in the composting process[7]. Several researches have shown that swine manure may contain high concentrations of Cu, Pb, Mn and Zn because of feed additives[8-10]. Cu and Zn are widely applied as additives to pig feed by pig raisers for shortening the duration of breeding, resulting in high concentrations of Cu and Zn in pig manure[10]. Most of these trace elements are retained mainly in the solid phase after solid–liquid separation from slurry. As such, successive application of Cu, Mn and Zn rich swine manure

(SSM) composts in to the agricultural field may cause metals to accumulate to toxic levels[8]. Lead occurs naturally in the environment but human activities also responsible for introducing lead in the soil[11]. Although, the heavy metal concentrations in sewage sludge or compost were far below the regulation standard but the long-term land application of compost with background heavy metal concentration can increase content and accumulation of the heavy metals in the soil[12]. Metal in soils can be divided into two fractions: i. inert fraction assumed as the non-toxic fraction, and ii. the labile fraction, assumed to be potentially toxic[13]. To assess the availability of heavy metals, only the soil labile fraction is taken into account because this fraction is often called as bioavailable fraction. However, the bioavailable fraction can differ from one metal to another and from one receptor to another. The availability of metals for plants and micro-organisms in soil depends on the composition of the different component of soil such as carbonates, (oxy) metal hydroxides, organic matter and silica[13]. The trace elements bioavailability has been considered as one of the most crucial problem in agricultural and environmental studies[14].

Zorpas et al[15] studied uptake of heavy metals by natural zeolite during sewage sludge composting and found that zeolites may be useful as metal scavengers in metal-rich sludges. It has the ability to exchange sodium and potassium. With increasing amounts of zeolite in the compost, the concentration of all heavy metals in the samples decreased while the concentration of sodium and potassium increased in the compost[15]. The agricultural utilization of tannery sludge compost implies knowing its degree of stability, as well as its content and biochemical forms of the heavy metals present[16]. Composted municipal solid waste is heterogeneous mixtures of organic and inorganic materials, many of which contain trace metals. Therefore this review examines the water solubility, DTPA extractability and leachability of heavy metals in the compost, which has to be applied to the agricultural field.

Bioavailability of Heavy Metals

Water-soluble metals: The water soluble fraction is positively the most biologically active. The water soluble fraction has highest potential of contamination of food chain, surface water and ground water[1]. Nickel is recognized as a potentially mobile and water-soluble element and the labile pool in compost is relatively easily solubilized by mild extractants due to the weaker binding to the matrix compared with other key metals which is also consistent with its behaviour in sewage sludge for example[17]. The water-soluble fraction of Zn, Pb, Cu and Cd were found to decrease and stabilize after the thermophilic stage of composting. The pH of compost just before the thermophilic stage was found to be acidic causing higher available Pb and Zn, which have higher water-extractable concentrations at low pH[2]. The increases in total metal concentrations during composting was not accompanied increase in the amount of water soluble Cu, Mn and Zn. Sequential changes in the water soluble fractions of Cu, Mn and Zn were reflected by changes in water soluble organic carbon concentrations, which increased to a maximum at day 18 of composting and then declined[8].

Fang and Wong[18] studied the changes in water-soluble Cu, Mn, Ni and Zn contents in sewage sludge co-composted with lime at day 0, 7, 21, 49 and 100 expressed as mg kg^{-1} dry sludge-sawdust mixture and reported that water-soluble Pb, Cr and Cd contents in all treatments were below the detection limits of 0.1, 0.1 and 0.02 mg l^{-1} for these elements. Fuentes et al[19] studied different types of sludges (aerobic, anaerobic, unstabilised and sludge from a waste stabilization pond) for water soluble heavy metals and reported that the water-soluble Pb was in all cases below 0.2 mg kg^{-1}. However, the quantity of water-soluble Ni was lower than 1 mg kg^{-1} for all sludges. Hsu and Lo[8] studied concentrations and water solubility of Cu, Mn and Zn in the composting of two swine manure was performed in two piles for 122 days, and reported that the water soluble fraction of Cu (expressed as percent of the total concentration in the sample) increased from 3% in the raw separated swine manure (SSM) to 5% at day 12, sharply increased to about 16% at Day 18 and gradually decreased to 3% in the compost. The water extractable fractions of Mn or Zn increased from 1% in the raw material to 2% at day 18 and then gradually decreased to 0.5% at the end of the process. These results indicate that composting substantially modifies Cu leachability in SSM compost and appears to have little influence on Mn or Zn leachability[8]. Lime is very effective amendment material for heavy metal immobilization in co-compost with sewage sludge[4]. Addition of lime caused a significant reduction in water-soluble Cu, Mn and Zn contents during composting process. Cu, Mn and Zn contents in the control increased slightly initially, and then rose sharply after day 21. Fang and Wong[18] performed a batch composting study to evaluate the feasibility of co-composting sewage sludge with lime at 0, 0.63, 1.0 and 1.63% w/w, and composted for 100 days in laboratory batch reactors to reduce the availability of heavy metals in the sludge compost and stated that the lime amendment was effective in reducing heavy metal availability of sludge compost by forming less soluble carbonate salts. Ni demonstrated a different pattern of change with a decrease in Ni content according to the increase in time for all treatments as compared to other three metals[18].

The metallic form of chromium is quite stable and can resist attacks from environmental processes. However, in either the trivalent or hexavalent forms, chromium exhibits higher chemical activity (including amphotericity, i.e., the ability to react chemically as an acid or a base), as well as solubility and hence potential mobility and subsequent removal from the solid fraction[16]. Ciavatta et al.[5] reported that Cr appears to be the heavy metal that tends to insolubilize during composting and thus to decrease in solubility in the absence of soil. Cr released from organic matter in neutral or alkaline soils precipitates as insoluble forms; therefore it is not adsorbed by plants. Due to its low solubility, only a little amount of chromium is bioavailable, meaning that even when crops are grown in soils treated with sludge relatively high in Cr, phytotoxicity is rarely observed.

Castaldi et al[20] reported that the water-soluble Pb decreased from 18.05 mg kg^{-1} in the raw MSW to 1.18 mg kg^{-1} at day 70, and gradually decreased to 0.89 mg kg^{-1} in the mature compost. The water-extractable fractions of Cd, Zn and Cu also decreased during composting process, reaching values of 1.36 mg kg^{-1}, 6.70 mg kg^{-1} and lower than 0.005 mg kg^{-1} for the Cd, Zn and Cu, respectively. Reduction of water-soluble fraction of heavy metals was 100% for Cu and about 60% for Cd and Zn.

The pH is considered 'master variable' controlling ion exchange, reduction/oxidation, adsorption and complexation reactions. Cations are adsorbed on organic matter at high pH[21]. The effect of organic matter amendments on heavy metal solubility also depend greatly upon the degree of humification of their organic matter and their effect upon soil pH[14]. The oxidation process and the formation of organo-metallic complexes taking place during the composting could reduce the soluble contents of Ni[18]. In a risk assessment, the pH is one of the factors that most affect the mobility and bioavailability of metals. The mobilization of pollutants depends on several factors: their mobility, their concentration in the soil and their solubility[13]. The solubility depends on the chemical composition of leachate in equilibrium with the material; this chemical composition is influenced by the variation of pH that moves the redox equilibrium to predominant forms[13]. At high pH, the predominant forms are hydroxides with low solubility and at low pH, free metallic ions which are highly soluble and predominated. There are two types of complexes in metal complexation reactions with soil particles: the soluble and the insoluble complexes. At pH 9 the solubility of copper is increases due to the formation of soluble complexes[13].

Diethylene triamine pentracetic acid (DTPA) extractable heavy metals: It has been considered that DTPA is a chelating agent and widely used for diagnosis of plant availability of the metals in soil at regular or even higher concentration[22]. The DTPA-extractable fraction of metals might represent a supplemental approach to check the bioavailability of heavy metals in the soil and sludge amended soil for plant uptake[3,18,23]. DTPA solution is assumed to extract both carbonate-bound and organically bound metal fractions in calcareous soils, and indicates the amount of metals potentially available for plant uptake[24]. The mobility of trace metals, their bioavailability and related eco-toxicity to plants, depend strongly on their specific chemical forms or ways of binding[14,24]. The metals bioavailability in the soil also depends on their distribution between solid and solution phases, dependent on the soil processes like cation exchange, specific adsorption, precipitation and complexation. The process of metal uptake and accumulation by different plants depend on the concentration of available metals, solubility progressions and the plant species growing on these soils[14]. The fate of toxic metal cations largely depends on their interactions with inorganic and organic soil surfaces. However, it is difficult to isolate the factors involved in heavy metal bioavailability, given different land uses and the great number of soil types[3]. The microbial component of soil has been scarcely considered as an important factor involved in metal bioavailability, even if microorganisms associated with soil organic fractions would be expected to have an active role in the mobilization equilibria of toxic metals. Microbial biomass represents a small fraction of soil organic matter, but plays a fundamental role in the cycle of all major plant nutrients and is very sensitive to modifications of soil equilibria[3].

Guan et al[21] studied availability of Cu with livestock manure, and concluded that the groups of –OH and –COOH supplied by livestock manure (LM) increased the binding sites and combined with Cu to form insoluble and immobile complexes, thus the concentration of free Cu^{2+} decreased and the potential environmental risk was reduced drastically. The reason should be attributed to three aspects: i. lager amount soluble organic ligands was derived from LM, hence the complexation of Cu with the ligands was more competitive than the adsorption to the soil organic matter ii. the soluble organic matter could increase the Cu availability by providing a strong buffer for free Cu^{2+} iii. higher level of LM can significantly increase the biomass of soil microorganisms which would enhance organic matter mineralization, thus increasing the potential Cu mobility in the soil. As a mineral element, Cu in the plants was derived from soil matrix; however, the potential behavior, bioavailability and the transfer dynamics of Cu in soil–plant system can be poorly predicted by the total content. It has been realized that the toxicity of Cu is determined by cupric ion activity; as a result, the mobile Cu is more toxic to the plant growth than strongly complex forms[22]. Bragato et al[3] studied DTPA extractable heavy metals in soil with 0 t ha^{-1}, 7.5 t $ha^{-1}$and 15 t ha $^{-1}$ sewage sludge addition and reported that in the control soil, DTPA solution extracted about 6% of total Zn, 3% of total Ni, 29% of total Cu and 24% of total Pb. DTPA-extractable Cu and Pb did not change significantly between the treatments, while DTPA-extractable Zn and Ni gradually increased in direct proportion to the amount of sewage sludge added to the soil. In the 7.5 t ha^{-1} sludge treatments, DTPA-extractable Zn represented about 9% and DTPA-extractable Ni about 4% of their total content in the soil. Larger amounts of total Zn and Ni, 11 and 5%, respectively, were extracted by DTPA in the soil treated with 15 t ha $^{-1}$ of sludge. Nomeda, et al[25] reported the bioavailability of Mn, Pb, and Zn except Cu increased during the composting process. The metal mobility in the composted mixture ranked in the following order: Mn > Zn > Pb > Cu.

Red mud amendment significantly reduced the mobility and plant availability of metals in municipal solid waste (MSW) compost when the red mud was added at the beginning of the composting process[26]. The lime amendment at 1% significantly reduced DTPA extractable metals. It is likely that the DTPA extractable heavy metals can form less soluble metal carbonates and hydroxides with lime and thereby reducing its availability[4]. Fang and Wong[18] reported that lime amendment significantly reduced DTPA-extractable metal contents. The maximum reductions were 60 and 40% for Cu, 80 and 40% for Mn, 55 and

10% for Zn, and 20 and 25% for Ni at the end of the composting period for the lime-amended sludge as compared to the control. Wong and Selvam[4] reported that after composting, the Cu, Mn, Ni and Pb and Zn contents decreased with an increase in lime amendment rate. The difference in Ni and Zn contents between control and lime treated composts was not significant. In the sludge, the order of metal contents in DTPA extracts was: Zn > Cu > Mn > Pb > Ni, but after composting the order was: Zn > Mn > Cu > Pb > Ni. Addition of lime also resulted in a decrease in the extractable Pb contents throughout the composting period. At the end of composting, the percentage of reduction of Pb contents for lime-amended sludge compost higher than control[18]. Chiang et al[12] reported that in case of added lime, the amount of DTPA-extractable Pb, Cu and Zn significantly decreased in the composting because of the higher ion exchange capacity and alkalinity. Fang and Wong[18] reported that a significant decrease in the initial extractable Ni content was only obtained at the high lime- amendment levels (51%). Lime-amended sludge compost followed a similar trend but with a lower Mn content at the end of composting[18].

Chen et al[10] investigated the effects of bamboo charcoal (BC) on nitrogen conservation and immobility of Cu and Zn during pile composting of pig manure and concluded that the extraction efficiency of DTPA extractable Cu and Zn also decreased with increasing amount of BC this means that BC was effective for reduction of bioavailability of Cu and Zn. It adsorb heavy metals due its large specific surface area, high surface density of functional groups and metal oxides, in addition, similar to other carbonaceous materials, BC has a large quantity of surface negative charge and a high charge density, which can also improve the adsorbing capacity of BC for positively charged heavy metal ions[10]. Hua et al[26] concluded that mobility of heavy metals in the sludge composting could also be reduced by the addition of BC. However, the stabilization effect of BC was different for Cu and Zn. DTPA-extractable contents of Cu and Zn in sludge composting material with 9% BC amendment dropped 27.5% and 8.2%, respectively, at the end of composting as compared with control. Chiang et al[12] investigated the effect of different amendments including lime, coal fly ash and natural zeolite on the potential for inhibition of heavy metal mobility during the sewage sludge composting process and reported that, the amounts of tested DTPA-metals decreased insignificantly using coal fly ash. In case of added zeolite and lime, because of the higher ion exchange capacity and alkalinity, the amount of DTPA-extractable Pb, Cu and Zn significantly decreased in the composting[12]. Fang and Wong[18] performed a batch composting study to evaluate the feasibility of co-composting sewage sludge with lime at 0, 0.63, 1.0 and 1.63% w/w, and composted for 100 days in laboratory batch reactors to reduce the availability of heavy metals in the sludge compost and reported that the percentages of reduction for DTPA-extractable Cu were 20, 30 and 40% in the order of increasing lime amendment. The DTPA-extractable Mn increased markedly in the first 50 days and then decreased slightly about 60 mg kg^{-1} in the control. No consistent trend could be observed for DTPA- extractable Ni and Pb contents in all treatments during the composting period. Extractable Ni increased considerably from 6.7 to 7.3 mg kg^{-1} within the first 7 days in the control. A significant decrease in the initial extractable Ni content was only obtained at the high lime- amendment levels (51%). The percentages of total contents for the five metals extracted by DTPA extractant varied from 22 to 34% for Cu, 34 to 38% for Mn, 12 to 22% for Ni, 21 to 35% for Pb and 35 to 46% for Zn. However, DTPA-extractable percentage of the control for Cu, Mn and Zn increased from 25, 34 and 38% at day 0 to 34, 38 and 45% at day 100, respectively, whereas Ni and Pb decreased from 20 and 35% at day 0 to 13 and 25% at day 100, respectively. Zn showed the highest extractable percentage of the total metal content and the highest DTPA-extractable content among all five metals[18].

Fuentes et al[19] reported that the contents of DTPA-extractable Cr were all below 2 mg kg^{-1}, indicating the low availability of Cr in all the sludges analyzed. It is necessary to stress the high percentage of DTPA-extractable Cd, mainly in the least mineralized sludges (unstabilised and aerobic sludge), which surpasses 30% of the total Cd content. In case of the anaerobic sludge, the amount of Cd available for plants was approximately 17% of the total. The DTPA extracted about 15% of total Cu and less than 9% of total Fe, which was the most abundant among all heavy metals studied. Ni presents a great bioavailability level for the four types of analyzed sludges. The DTPA extraction results showed that about 37% of total Ni in unsterilized sludge was available, while 23%, 17% and 14% was plant available for anaerobic, waste stabilization pond (WSP) and aerobic sludge, respectively. The concentration of total Pb in the sludges varied from 251 mg kg^{-1} for the WSP sludge to 58 mg/kg for the aerobic sludge. The quantity of Pb mobilized in DTPA extraction for the unsterilized sludge was higher than 33%, while 12% was plant available for the rest of sludges. The concentrations of total Zn in WSP and anaerobic sludges were about double of the aerobic and non-stabilized sludge. The content of DTPA-extractable Zn was higher in the least stabilized sludge (37% and 27% for un-stabilized and aerobic sludge, respectively) than in the anaerobic (14%) and WSP (11%) sludges. Phytotoxicity could be caused by this high Zn bioavailability[19].

Leachable Heavy Metals

The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphasic wastes. If an analysis of any one of the liquid fractions of the TCLP extract indicates that regulated heavy metals are present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for those metals, then the waste is hazardous[28]. TCLP is used to determine the suitability of compost for land application or should be considered a hazardous waste. The procedure is designed to simulate the leaching potential of the compost material when it is applied to soil. The regulatory limits for leached toxic heavy metals are based on avoiding groundwater contamination that would create a risk to human and environmental health[29]. The threshold limit for heavy metals contamination in mg/kg is given in table 1. The heavy metal leached fraction concept, defined as the ratio of the amount of a heavy metal released from TCLP test to its total content, is commonly used to assess the leachability of heavy metals in the compost[12].

Table-1
Threshold limits for heavy metals[28]

Contaminants	Threshold (mg/kg)
Arsenic	100
Barium	2000
Cadmium	20
Chromium	100
Lead	100
Mercury	4
Selenium	20
Silver	100

Note: Only applicable to samples which are 100% solid.

The mobility, bioavailability and eco-toxicity of the metals depend on the specific chemical forms or bindings in which the metals exist in different waste materials. It is very much necessary to examine leachability of heavy metals to determine the suitability of decontaminated sludge for land application[30]. Wang et al.[31] studied leachability of Cu in chicken manure compost during the 110 days of composting period and reported that the amount of leached Cu increased initially but at the end of composting process it was reduced significantly. The amount of Cu leached from manure throughout the composting process averaged 20% of the total Cu in the compost[32]. The Ni was present at much higher water soluble levels in MSW compost and considered as leachable[2].

An acid neutralization capacity test in order to estimate the metal leachability in the compost produced by using clinoptilolite as additive and reported that by increasing the leachate pH, the heavy metal concentration decreased[32]. Ciba et al[33] reported that zinc can be leached in significant amounts, and only if pH is 2.5. As expected, leaching at pH 2.5 enables higher amounts of elements to be leached than at pH 4.5. This seems to be especially understandable in the case of metals chemically bound as carbonates. In the case of zinc, it can be seen that at lower pH a substantial percentage of this form can also be extracted. Chiang et al[12] revealed that the leached fraction of Cu, Zn and Ni decreased with increasing co-composting time. In all additive tests, the leached fraction of Zn was higher than that with other tested metals. Since the total Zn concentration was high in co-compost and most soluble Zn was leachable. Although the tested additives had higher alkalinity, larger surface sites and ion exchange ability for inhibiting the heavy metal mobility, the additives might not suppress the changes in Zn leaching[12].

Conclusion

Composting process can reduced toxicity of metals by reducing available fractions such as water soluble, DTPA extractable and leachable fractions. Toxicity of heavy metals depends on biavailable and leachable fraction rather than its total concentration in the compost and amended soil. The water soluble fraction has highest potential of contamination to the food chain, surface water and ground water. The process of composting can promote the complexation of heavy metals whose mobility and availability tend to decreases with decreasing toxicity. In a risk assessment, pH is of the most important factor that affects mobility and bioavailability of metals during the composting process. Addition of lime during composting process reduced water solubility of heavy metals by increase pH. Natural zeolites have potential for metal immobilization due to their high ion exchange capacities and highly porous structures. Care should be taken when using zeolites with high sodium content as they have been shown to increase soil salinity and exchangeable sodium concentrations, which could cause plant toxicity. Bamboo charcoal reduced bioavailability and leachability of heavy metals due to it has a large quantity of surface negative charge and a high charge density. This study suggested that bioavailability and leachability of metals should be assessed before addition compost (derived from sewage sludge, municipal solid waste, tannery waste etc.) to the agricultural field. There is very little information available on bioavailability and leachability of Hg, As, Ba, Se and Ag in the composts, therefore the more study required about bioavailability and leachability of these metals in the compost.

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