

# Sources, Bioavailability and Fate of Heavy Metals and Organic Contaminants in Compost Manure

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## ABSTRACT

This paper reviews the sources, bioavailability and fate of heavy metals and organic contaminants in compost manure and in soils of which the manure is applied. The toxicity of heavy metals and organic compounds in soil of which would have come from applied compost is also discussed. Type of materials, their background and where collected for use in composting contribute to the sources of heavy metals and organic compounds in compost manure. The materials that are major sources include sawdust, sewage sludge and municipal solid waste (MSW). Sewage sludge usually is collected from wastewater and or sewage treatment plants while sawdust is collected from timber industries that manufacture different items from raw wood. MSW is found at municipal operated landfills and dumping facilities. Both inorganic and organic contaminants are highest in sewage sludge because of enrichment that occurs during wastewater treatment process. Heavy metals such as iron (Fe), manganese (Mn), chromium (Cr), nickel (Ni), zinc (Zn) and copper (Cu) are found in sawdust and come from wood cutting metal component. The extent of heavy metals and organic compounds in sewage sludge depends on the type of wastewater being treated. Sewage sludge from industrial wastewater treatment plants has generally higher levels of heavy metals (copper, zinc, lead, iron, cobalt, nickel, chromium, cadmium) and organic compounds (polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins/furans and polyaromatic hydrocarbons) than that from household wastewater treatment plants. Electronic waste, metal (soft drink cans) and glass (food bottles) components in MSW are the major contributor to heavy metals. Source separation of the biodegradable waste from electronic waste, metal and glass components in MSW has been observed to reduce the level of Cu, Zn, Lead (Pb) and Fe in compost. Bioavailability and toxicity are influenced by factors such as type and amount of contaminant in the soil and compost, type of soil, amount of organic matter in the compost and other environmental conditions such as pH.

**Keywords:** agriculture, pollutants, soil conditioner, transport

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## INTRODUCTION

Composting can be defined as the controlled decomposition of organic matter (OM) to produce humus or manure. It can also be described as a stabilization process of aerobic decomposition, which has been widely used for different types of biodegradable wastes (Cai *et al.* 2007). Anaerobic and aerobic microorganisms decompose OM and narrow down the C: N ratio of the refuse. The same process occurs in natural systems when humus is produced as the plant material grows, dies and decomposes in the soil (NRAES 1992). Compost manure is currently being used as an inexpensive and simple solution for a wide variety of environmental and socio-economic problems. A lot of research has been done

on the benefits of compost manure (Pinamonti *et al.* 1997; Garcia-Gil *et al.* 2000; Kiikkila *et al.* 2002; Jordao *et al.* 2003; Wong and Selvam. 2006; Mbarki *et al.* 2008). Pinamonti *et al.* (1997) and Garcia-Gil *et al.* (2000) both indicated that compost manure increases porosity, structural stability, available water content, soil fertility and reduction of erosion when applied to the soil. Additionally, Pinamonti *et al.* (1997) indicated that compost manure disturbs soil very little, preserves its biological activity, increases its OM content, conserves its moisture and favours root aeration. Compost manure further has been praised for reducing air pollution and solid waste from olive trees in Greece (Manios *et al.* 2004). Studies done by Rynk (2003) indicated that compost could be used to remediate a landfill and turn

it into a national park. The effects of compost on stream bank stabilization in Oconee River at Ben Burton Park in Athens, Greece have been reported (Faucette and Ruhlman 2004).

Apart from the importance and benefits of compost manure in the environment, compost manure has some detrimental impacts as well (Ng *et al.* 2008; Oleszczuk 2008). Garcia-Gil *et al.* (2000) and Jordao *et al.* (2003) indicated that compost manure increases the level of potentially harmful trace metals and various persistent organic toxins in the soil and plants. These contaminants leach through the soil; they may also contaminate ground water. Heavy metals and persistent organic compounds absorbed by plants pose health effects on humans due to their toxicity, persistence and bioaccumulation in the food chain. Under certain environmental conditions, contaminants may accumulate to a toxic concentration and cause ecological damage (Karadede and Unlu 2000).

The level of contaminants in compost is influenced by the type of materials used to make it which determines the quality of compost manure (Manungufala *et al.* 2008). This means that the source, environment and condition from where the compost material has been grown contribute to the quality of the compost manure. For example, compost manure made from crop residues that have been fertilized with sewage sludge and some trace metal salts have high concentrations of heavy metals (Jordao *et al.* 2003). Compost materials that have been exposed to smelter emissions and vehicle exhaust fumes mostly have high trace metal concentration, for example, lead (Pb) and cadmium (Cd) (DWA 1996). It is mostly the labile or bioavailable fraction of the contaminant that is responsible for toxicity. Several factors contribute to the levels of labile metals in the environment such as soil pH level, amount of organic matter, type of soil and type and amount of contaminant, etc. With the exception of lead and copper, solubility and lability of most heavy metals have been found to be inversely related to pH (Giusquiani *et al.* 1995). A cumulative research in Europe into the agronomic use of compost discovered that heavy metals tend to accumulate in soil and plants in the following order: zinc (Zn) > copper (Cu) > Pb > Cd > nickel (Ni) > chromium (Cr) (Pinamonti *et al.* 1997). Heavy metals are reported to inhibit nitrification and denitrification processes (Waara 1992) and reduce microbial oxidation of organic compounds (Madoni *et al.* 1996).

This mini-review highlights the common sources of contaminants in compost manure, their bioavailability, fate and toxicity. Bioavailability and toxicity is somewhat interlinked since the contaminant has to be bioavailable before it is taken up by organisms and/or plants.

## SOURCES OF CONTAMINANTS IN THE COMPOST

### Sawdust

Manungufala *et al.* (2008) conducted a detailed study on the levels of metals in compost manure made by communities in South Africa. Further, different materials used to make compost manure were also evaluated for the presence and levels of metals. Sawdust was found to be the major source of heavy metals. The levels of heavy metals were found in the following order; iron (Fe) > manganese (Mn) > Cr > Ni > Zn > Cu > cobalt (Co) > Cd. This was attributed to the metal used in cutting the wood. On the other hand, cabbage

leaves were found to be the major source of essential metals for human growth, for example calcium (Ca) and magnesium (Mg) build strong bones, teeth and nails. The order of essential metals could be arranged in the following order; Ca > Mg > potassium (K) > sodium (Na) > lithium (Li). In this study the levels of organic contaminants especially pesticides were not investigated. Hseu (2004) also compared the level of heavy metals in wood compost residues to poultry litter, food waste, municipal sewage sludge waste, etc. by looking at different digestion methods. Wood waste had the third highest amount of Cd with poultry litter having highest value followed by municipal solid waste. For Cr, wood residues had second highest amount to food waste. The same trend was observed for Pb and Mn. Wong and Selvam (2006) found high levels of Zn in saw dust but very low compared to the levels determined in sewage sludge. Ng *et al.* (2008) did a study of polychlorinated di-benzo-*p*-dioxins/furans (PCDD/Fs) and polychlorinated bi-phenyls (PCBs) in livestock waste (pig manure) compost containing saw dust. The source of these compounds was attributed to sawdust/wooden pellets as part of the wood preservatives impurities.

### Sewage sludge

Sewage sludge is commonly used in composting because of its relative abundance from wastewater treatment plants. However, a major concern of using sewage sludge as a compost is potential contaminants that are enriched in the sewage sludge during the process of separation of solids from the wastewater. Some countries therefore prohibit the use of sewage sludge as fertilizer that exceeds the maximum values allowed for total concentrations of heavy metals (Pereira and Kuch 2005). Highly toxic metals such as mercury (Hg) and Cd have lowest maximum allowed values in the sewage sludge for agriculture use (Table 1).

The extent of contaminants in the sewage sludge depends on the type of treatment plant, whether it treats only household wastewater and/or industrial wastewater (Pereira and Kuch 2005; Dai *et al.* 2007). Industrial wastewater generally has high amounts of contaminants which later get enriched in the sludge Table 2 shows that the levels of the common heavy metals can be arranged in the following decreasing order; Zn > Cu > Cr > Pb > Ni > Fe > Hg > Cd. The order reflects the widespread use of the metals.

Dai *et al.* (2007) compared the levels of PCDD/F, Polycyclic aromatic hydrocarbon (PAH) and heavy metals in the sewage sludge from six different wastewater treatment plants in Beijing, China. The concentration (mg kg<sup>-1</sup>) of the metals varied from plant to plant but levels of Hg (17.0-23.4), Zn (783.4-3096.3) and Cd (5.9-13.0) exceeded the maximum permitted content limits for soil with pH less than 6.5. The maximum permitted concentration (mg kg<sup>-1</sup>) for the sewage sludge used for soil with pH less than 6.5 in China is 5 for Hg and Cd and 2000 for Zn. The source of Hg was attributed to sterilizations in hospital and household used in Beijing. Zn was attributed to industrial source especially steel industry. A number of PAHs categorized as priority pollutants by US EPA were also detected in sludge from the six treatment plants. The concentration (µg kg<sup>-1</sup>) ranged from 2467-25923. Wastewater from a steel and dyeing industrial wastewater treatment plant gave the highest concentration. The source from other treatment plants was suspected to come from fuel industry discharge because both

**Table 1** International legislation concerning the levels of heavy metals in sewage sludge and final disposition.

	Metal						
	Nickel	Copper	Lead	Zinc	Chromium	Cadmium	Mercury
Germany (Agriculture)	50	60	100	200	100	1.5	1.0
Germany (Landfill)	200	1200	1200	3000	1200	20	25
EUA (Agriculture)	210	750	1500	1400	1500	20	8.0
Brazil (Agriculture)	25-40	91-190	80-100	470-1512	44-73	1-3	1.5-2.5

Source: Pereira MS, Kuch B (2005) Heavy metals, PCDD/F and PCB in sewage sludge samples from two wastewater treatment facilities in Rio de Janeiro State, Brazil. *Chemosphere* 60, 844-853, with kind permission of Elsevier, Ltd., ©2005.

**Table 2** Example of concentration of heavy metals (mg kg<sup>-1</sup>) found in sewage sludge.

Sludge type	Ni	Cu	Pb	Zn	Cr	Cd	Hg	Fe	Reference
D, AE	198	1187	267	1999	615	44	7.0	-	Bridle <i>et al.</i> 1990
D, AE	111	217	119	779	229	4.3	N.D	5.9	Skrypski-Mantele 1992 <sup>1</sup>
A, AE	N.D	519	73	1310	N.D	3.3	N.D	-	Carlson-Erval and Morrison 1997
D, AE	81	401	343	1340	125	N.D	N.D	-	Muller 1998 <sup>1</sup>
D, AN	94	299	119	1070	190	N.D	N.D	-	Muller 1998 <sup>1</sup>
A,AE	67.8	226.3	110.7	1387.7	39.2	2.7	7.97	19.7	Pereira and Kuch 2005
D,M	11.8	271.1	51.4	672.0	9.5	1.2	4.31	9.1	Pereira and Kuch 2005
D, AN	108.1	649.7	88.8	1310.0	115.0	4.0	N.D	60.1	Pereira and Kuch 2005
AN	49.9	229.0	57.5	1431.4	57.8	7.0	21.8	-	Dai <i>et al.</i> 2007
A	60.0	394.5	95	3096.3	54.8	9.3	24.0	-	Dai <i>et al.</i> 2007
Mean	86.4	439.4	132.4	1439.5	159.5	9.5	13.0	23.7	

D = digested, A = activated, AE= aerobic, AN = anaerobic, M (AE + AN), N.D = not detected. <sup>1</sup> = as cited by Pereira and Kuch 2005.

domestic and industrial wastewater was being treated. Another study compared the levels of heavy metals, PCDD/F and PCB in sewage sludge samples from two wastewater treatment facilities, one urban and one rural, in Rio de Janeiro State, Brazil to one in Germany (Pereira and Kuch 2005). The sludge samples in general showed low concentration regarding PCDD/F ( $\Sigma$ TCDD/F-OCDD/F) with values ranging from 1313.0-4149.0 pg g<sup>-1</sup>. The toxicity equivalent concentrations were between 3.2-98.9 pg I-TEQ/g and 2.3-128.5 pg I-TEQ/g according to NATO/CCMS and WHO, respectively. On the other hand, the mean values for the Germany (Baden-Wurtemberg) wastewater sludge was 12.8 I-TEQ/g and 11.0 I-TEQ/g according to NATO/CCMS and WHO, respectively.

The PCDD/F congene profiles found in Brazilian samples indicated that urban sewage sludge has both chlorophenols and depositional sources that seemed to contribute to contamination pool. PCB was attributed to contamination stemming from technical PCB formulations.

In a study by Amir *et al.* (2005) a substantial amount of heavy metals during the composting process of Moroccan sewage sludge were found. The order of total metal concentrations (mg kg<sup>-1</sup>) was found as follows; Zn (~275-230) > Pb (~140-110) > Cu (~ 60-75) > Ni (~25). The total concentrations decreased during composting except for Ni. The decrease was more pronounced after 30 days of composting. In another study, it was reported that sewage sludge increased the levels of heavy metals, particularly Cd, in the soil, after the soil was treated with sewage sludge compost manure (During *et al.* 2003). Because of enrichment of the metals in the sludge during wastewater treatment, the total heavy metal content in sewage sludge is about 0.5-2% on a dry weight basis (Wong and Selvam 2006). Cai *et al.* (2007) found concentrations of Cu and Zn exceeding the acceptable values for agricultural use.

Sorme and Lagerkvist (2002) carried out a detailed assessment of sources of heavy metals in urban wastewater in Stockholm, Sweden. This study is important because it also gives an idea of the sources of heavy metals in sewage sludge where enrichment finally occurs. In this case the sources of sewage water and stormwater were categorized to enable comparison with other research and measurements

(Sorme and Lagerkvist 2002). Households, drainage water, businesses, pipe sediment (all transported in sewage water), atmospheric deposition, traffic, building materials and pipe sediment (transported in storm water) were identified as different categories. The largest sources of Cu were found to be tap water and roofs while galvanized material and car washes were sources of Zn. Chemicals used in wastewater treatment plant and drinking water were the largest sources of Ni. The largest source of Hg was the amalgam in teeth while Pb, Cr and Cd sources were poorly understood.

### Municipal solid waste

Municipal solid waste (MSW) is also commonly used as compost (Epstein *et al.* 1992; Richard and Woodbury 1992; Veecken and Hamelers 2002). A review on the use of composted municipal solid waste in agriculture has also been reported (Hargreaves *et al.* 2008). MSW is largely made up of kitchen (food left overs, coffee filters) and yard wastes (flowers, grass, leaves and branches) which makes it attractive for composting because it is easily biodegraded by microorganisms. Composting is also advocated as a major potential MSW management practice by municipalities in many countries. However, like any other material for compost, the concern is toxic contaminants found in various constituents of MSW (Epstein *et al.* 1992; Sorme and Lagerkvist 2002; Veecken and Hamelers 2002). Food left overs as example has been cited to contain Cu and Zn (Sorme and Lagerkvist 2002). The situation is compounded in cases where source separation of MSW is not performed (Epstein *et al.* 1992). This means that other non biodegradable wastes such as batteries, toys and other metallic household wastes come into contact with the biodegradable waste thus increasing the levels of pollutants in the latter. Both Richard and Woodbury (1992) and Epstein *et al.* (1992) investigated the impact of MSW separation on heavy metal contaminants in solid waste composts. Epstein *et al.* (1992) looked at facilities in United States and European Union. The concentration of heavy metals in source separated wastes (SOW) were somewhat lower than in mixed MSW compost but both did not pose a risk to human health or environment. The research found no significant differences

**Table 3** Effect of different contaminant separation methods on the heavy metal content ( $\mu\text{g g}^{-1}$  on a dry weight basis; values = means  $\pm$  SD) of MSW composts in Europe and North America.

Metal	Europe			North America		
	Sorting method		% difference	Sorting method		% difference
	Central	Source		Central	Source	
Cadmium	3.9 $\pm$ 0.4	1.2 $\pm$ 0.2	69	3.7 $\pm$ 0.4	1.1 $\pm$ 0.2	70
Chromium	117 $\pm$ 18	39 $\pm$ 9	67	29 $\pm$ 7	15 $\pm$ 5	48
Copper	354 $\pm$ 53	53 $\pm$ 11	85	349 $\pm$ 67	64 $\pm$ 20	81
Mercury	2.6 $\pm$ 0.3	0.7 $\pm$ 0.5	73	1.6 $\pm$ 0.4	1.0 $\pm$ 0.0	38
Nickel	63 $\pm$ 14	25 $\pm$ 6	60	31 $\pm$ 6	8 $\pm$ 2	74
Lead	565 $\pm$ 46	98 $\pm$ 13	83	324 $\pm$ 55	74 $\pm$ 28	77
Zinc	864 $\pm$ 83	282 $\pm$ 53	67	771 $\pm$ 141	292 $\pm$ 131	62
Mean			72			64

Source: Richard ML, Woodbury PB (1992) The impact of separation on heavy metal contaminants in municipal solid waste composts. *Biomass and Bioenergy* 3, 195-211, with kind permission of Elsevier, Ltd., ©1992.

for Cr between SOW and mixed MSW compost. However significant differences were observed for Cd at the 5% level and for Pb, and for Cu and Zn at the 1% level. The study by Richard and Woodbury (1992) found a considerable reduction in heavy metals in source separated compared to centrally separated MSW compost for Europe and North America (Table 3). The mean percentage differences for various common heavy metals were above 60%. This means that separation is most effective at an early stage of processing. In this case, batteries were identified as the major source of metal contaminants. Others are consumer electronics, ceramics, plastics, glass, light bulbs and bulb sockets, lead foils such as wine bottle closures, house dust, etc. All these must be separated from the kitchen and yard wastes to reduce the level of metals in MSW compost preferably at the source.

Veeken and Hamelers (2002) did a detailed study on the levels of Cd, Cu, Pb and Zn in source separated biowaste, the organic fraction of MSW. They found that the levels of these metals were similar to natural background content of biowaste constituents. This study also highlighted the benefits of source separation of MSW for composting.

### Other sources of pollutants for compost

Hsu (2004) identified soya bean meal, wood residues, guano, fish bone meal, food waste; poultry litter and flesh bone meal as other sources of heavy metals in the compost in the work on the evaluation of heavy metals contents in nine composts using four digestion methods. Hsu and Lo (2001) assessed the characterization and leaching of Cu, Mn and Zn from swine manure. Their results confirmed that swine manure can be a source of heavy metals in compost manure. Cu and Zn were found in high concentrations in swine manure. Artificial supplements in pig diets to promote growth e.g. a supplement of copper in pig diets accelerates weight gain and increases food conversion rates of fattening pigs are some of the sources of metals in pig manure. Fertilizers used in crop production contain trace elements either added intentionally or as impurities. These are capable of enrichment in plants/crops that when used as compost is a source of trace metals (Wong 1985a).

### BIOAVAILABILITY AND FATE OF METALS AND ORGANIC CONTAMINANTS IN COMPOST MANURE AND MANURE APPLIED SOIL

The process, materials and climate determines the bioavailability and fate of heavy metals and organic contaminants in the compost. The bioavailability fraction of the contaminant represent the part that can be taken up by plants or living organisms when exposed to it. For metal ions, depending on the state or charge which is influenced by environmental conditions, it can exist as free/exchangeable in compost, bound to carbonates, bound to Fe and Mn oxides and organic matter (Tessier *et al.* 1979). Most studies of the bioavailable and fate of heavy metals in compost have used the Community Bureau of Reference (BCR) extraction method which is a standardized method developed by a group of experts working under the auspices of the Commission of the European Communities (Mossop and Davidson 2003). Ideally, sequential extraction procedures selectively extract metals bound to specific soil fractions with minimal effect on other soil components (Mossop and Davidson 2003; Silveira *et al.* 2006). The selected reagents selectively react with different major components of the matrix releasing the associated heavy metals. Reagents ranged from mild to harsh were chosen in the sequential extraction to get released the metals according to the degree of metals bound with the matrices. Loosely bound or free heavy metals are extracted first while tightly bound to organic matter to be extracted at last. This means that generally amount of organic matter and inorganic minerals have a profound influence on the fate of metals in compost manure. A detailed review has recently been reported on the bioavailability and impacts of heavy metals in municipal solid waste composts

compared to sewage sludge (Smith 2009). In this review, it is argued that there is good experimental evidence demonstrating the reduced bioavailability and crop uptake of metals from composted MSW compared to other types of sewage sludge. Therefore composting processes overall are likely to lower the availability of metals in amended soil compared to other biostabilization techniques. The availability of metal 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 metal in the compost and the soil, and the ability of the plant to regulate the uptake of a particular metal (Amir *et al.* 2005). The total metal concentration in compost is important in controlling plant uptake of labile metals. This is because plant available fraction in soils increases with total metal in compost. This means that source separated waste with low metal content and green composts are likely to have inherently lower metal availabilities overall, compared to composted residues with larger metal content.

### Bioavailability and fate of metals in compost manure

Hsu and Lo (2001) studied the effect of composting on the characterization and leaching of Cu, Mn and Zn from swine manure. The research focused on how these metals would behave and associate with the matrix components for 122 days of composting. Total metal concentrations in the final compost increased almost 2.7-fold due to decomposition of organic matter, thus resulting in enrichment (Hsu and Lo 2001). A sequential extraction procedure was also performed to evaluate the humification process and partitioning of metals into water soluble, exchangeable, organically complexed, organically bound, solid particulate and residual fractions. Water was used to extract the water soluble, potassium chloride for the exchangeable, pyrophosphate for the organically complexed, sodium hydroxide for the organically bound and nitric acid for the solid particulates (Hsu and Lo 2001). Changes in the water-soluble fractions of Cu, Mn and Zn during composting process were reflected by water soluble organic carbon concentrations which rapidly increased to a maximum up until day 18 and then declined thereafter. However, during composting, major parts of the heavy metals were in the organically bound, solid particulate and organically complexed fractions, respectively. Heavy metal distributions in different chemical fractions were found to be independent of composting age and total metal concentrations in the compost. A similar study has also been reported by Amir *et al.* (2005). Sequential extraction was used to study the distribution of heavy metals during the composting of sewage sludge. In this case potassium nitrate was used to extract the exchangeable mobile fraction followed by water for the soluble mobile fraction, sodium hydroxide for the organically bound (mobilisable) and ethylene diamine tetraacetic acid (EDTA) for the organically complexed or carbonates mobilisable and nitric acid for sulfides mobilisable. A large proportion of heavy metals were associated to the residual fraction (70-80%) and more resistant fractions to extractions (X-NaOH, X-EDTA, X-HNO<sub>3</sub>) which accounts 12-29%. Less than 2% of the metals were bound to bioavailable fractions (X-KNO<sub>3</sub>, X-H<sub>2</sub>O). Bioavailable fractions during composting which depends on the heavy metal and physico-chemical properties of the medium decreased for metals with composting process except Ni-H<sub>2</sub>O. Zn and Cu were found to have more affinity to organic and carbonate fractions. Lead on the other hand preferred to bind more to sulfide forms, i.e., X-HNO<sub>3</sub>. Significant correlation was also observed between heavy metal fractions and changes to parameters such as pH, organic matter and humic substances during composting (Table 4). The decrease of Zn-KNO<sub>3</sub> fraction was significantly positive correlated with the decrease of organic (R = 0.86 \*\*) and the decrease of ash (R=-0.86\*\*), and Zn-NaOH and Zn-EDTA were well correlated with humic substances (Table 4). This means that the transformation of raw organic matter

**Table 4** Linear correlation coefficients of heavy metal fractions (copper, zinc and nickel) and total content with ash, humic substances (HS), pH and organic matter contents (OM) of sewage sludge during treatment by composting.

Heavy metal fraction	Ash	Humic substances	pH	OM
Zn-KNO <sub>3</sub>	-0.86**	0.09ns	0.48ns	0.86**
Zn-H <sub>2</sub> O	-0.26	0.72*	-0.21ns	0.21ns
Zn-NaOH	0.31	0.98**	-0.74*	-0.30ns
Zn-EDTA	0.09	0.90**	-0.58	-0.06ns
Zn-HNO <sub>3</sub>	-0.38	0.67	-0.14ns	0.39ns
Zn-total	-0.93**	-0.07ns	0.62	0.93**
Cu-KNO <sub>3</sub>	0.09	0.93**	-0.56ns	-0.12ns
Cu-H <sub>2</sub> O	-0.75*	-0.90**	0.98**	0.73*
Cu-NaOH	0.45	0.73*	-0.62*	-0.53ns
Cu-EDTA	0.59	0.93**	-0.86**	-0.63
Cu-HNO <sub>3</sub>	-0.05	0.88**	-0.46ns	0.03ns
Cu-total	-0.81*	0.09ns	0.40ns	0.83*
Ni-KNO <sub>3</sub>	-0.43	0.64	-0.1ns	0.42ns
Ni-H <sub>2</sub> O	0.90**	0.74*	-0.99**	-0.89**
Ni-NaOH	-0.90**	0.02ns	0.53ns	0.90**
Ni-EDTA	0.34	0.91**	-0.68	-0.4ns
Ni-HNO <sub>3</sub>	0.69	0.92**	-0.96***	-0.67
Ni-total	-0.62	-0.03ns	0.44ns	0.53ns

\*, \*\*, \*\*\*, ns: statistically significant at the probability level of 0.05, 0.01 and 0.001 and non-significant, respectively.

Source: Amir S, Hafidi M, Merlina G, Revel J (2005) Sequential extraction of heavy metals during composting of sewage sludge. *Chemosphere* 59, 801-810, with kind permission of Elsevier, Ltd., ©2005.

to stable humic substances during composting process allows the transformation of Zn from exchangeable to stable organic forms. **Table 4** also show good correlations between the decrease of Cu-H<sub>2</sub>O and the increase in humic substances ( $R = -0.90^{**}$ ), and the decrease of pH ( $R = 0.98^{***}$ ). Cu is known to have affinity to organic acids which contributes to the formation of humic substances. Cu-EDTA and humic substances also indicate good correlation ( $R = 0.93^{**}$ ).

Another study by Cai *et al.* (2007) looked at the total concentration and speciation of heavy metals in six different sewage sludge composts. The sludge was retrieved from two wastewater treatment plants in China. Enrichment of metals in the compost after 56 days of composting was observed. The concentrations increased by 12-60% for Cd, 8-17% for Cu, 15-43% for Pb and 14-44% for Zn compared to those in sewage sludge. The total concentrations of individual or total heavy metals in the final compost exceeded the maximum permissible limits proposed for compost or fertilizer (Cai *et al.* 2007). Sequential extraction was also performed on the final compost using acetic acid for water soluble and exchangeable fraction, mixture of ammonia hydroxide and hydrochloric acid for the iron-manganese oxide (FeMnOX) bound fraction, peroxide for the OM bound and finally the residue was extracted with hydrofluoric acid and hydroperchloric acid mixture. 70% of the total Cu was associated with organic matter-bound fraction while Zn was mainly concentrated in exchangeable and iron-manganese oxide bound fraction which implied the high mobility and bioavailability (Cai *et al.* 2007). The study also found out that continuously aerated composting treatment exhibited better compost quality and lower potential for lower toxicity of heavy metals where as inoculant with microorganism and enzyme spiked during composting had no obvious advantage on humification of organic matter and on reducing heavy metal mobility and bioavailability (Cai *et al.* 2007).

Some studies have investigated the effects of the addition of lime and/or sodium sulfide on the chemical speciation of heavy metals in compost manure (Wong and Selvam 2006; Wang *et al.* 2007). Wong and Selvam (2006) found that the addition of lime did not cause any changes in the different forms of Cu and Mn but the composting process caused transformations of residual form of Cu and Mn into

oxidizable and reducible form respectively. For Ni the reducible form was mainly transformed into residual form and lime addition decreased this change. Residual forms of lead increased with lime addition. The predominant residue form of Zn was mainly transformed into oxidizable form and lime addition reduced this change. Lime addition generally decreased the DTPA extractable heavy metal and therefore was concluded that co-composting of lime with sewage sludge could reduce the availability of heavy metals. The same observations were noted in a study by Wang *et al.* (2007) on the effects co-composting sewage sludge with sodium sulfide and lime.

### Bioavailability and fate of heavy metals in soil applied with compost manure

Pichtel and Anderson (1997) investigated the trace metal bioavailability in MSW and sewage sludge composts to plants. A sequential extraction procedure was used to determine the soil fraction and assess the plant availability of Cr, Cu, Ni, Pb and Zn in Glynwood (collected from east-central Indiana) silt loam amended with five different rates of composted MSW or composted sewage sludge. The application of the composts tended to shift the solid phase forms of the metals away from those extractable with nitric acid to more extractable with sodium hydroxide and ethylene diamine tetraacetic acid. More labile and free fractions of potassium nitrate and water extractable of the metals typically decreased with application of composted MSW and composted sewage sludge. Another study by Kiikkila *et al.* (2002) investigated the potential of organic material as copper immobilizing agent. For this purpose, composted sewage sludge, compost of organic household waste, a mixture of compost and woodchips, a mixture of compost and bark chips, garden soil, birch leaves, humus or peat was applied on the surface of a polluted soil and changes observed over a 16 month period. Copper fractions, Cu<sup>2+</sup> and complexed Cu and toxicity of the soil to bacteria, bacteria growth rate, number of bacteria cells and bacteria Cu tolerance was determined on samples. Sewage sludge, compost, the compost mixtures, and garden soil decreased the exchangeable Cu concentration in the polluted soil but had no effect on microbial activities, bacterial tolerance to copper or on the structure of the microbial community directly attributable to remediation (Kiikkila *et al.* 2002). The studies suggest that in polluted soil, application of compost could reduce the bioavailability of Cu to plants or other organisms. This is in agreement with observations by Pichtel and Anderson (1997).

Other studies have also been reported on the phytoavailability and fractionation of heavy metals in compost manure when applied to agricultural soil as soil conditioner (During *et al.* 2003; Zheljzakov and Warman 2004; Clemente *et al.* 2006; van Herwijnen *et al.* 2007). In the study by van Herwijnen *et al.* 2007 the effect of organic materials (four different composts) and a liming product containing organic matter (LimeX70) on the mobility and toxicity of metals in contaminated soils were investigated. Toxicity results showed significant reduction of metal bioavailability and toxicity for Greek cress, earthworms and bacteria. However, leaching tests showed that spent mushroom compost caused an increase in metal concentration in the leachates while LimeX70 caused a decrease. A generic conclusion could not be drawn because of the high variation in behavior between different amendments of each soil. In the study, four different composts and a liming product containing organic matter (Lime X70) were tested to examine both their metal retention and toxicity reduction capabilities on three different contaminated soils. Leaching test on a plant growth with Greek cress (*Lepidium sativum*), earthworm (*Eisenia fetida*) survival, condition test and a bacterial toxicity test using *Vibrio fischeri* were carried out. Zheljzakov and Warman (2004) conducted two experiments to evaluate the effect of compost addition to soil on fractionation and bioavailability of Cu, Mn, and Zn to four crops (*Beta vulgaris*

var. *ciela* L. - swiss chard, *Ocimum basilicum* L. - basil, Anthem *graveolens* - dill, and *Mentha X piperita* L. - peppermint). Swiss chard (*Beta vulgaris* var. *ciela* L.) and basil (*Ocimum basilicum* L.) were grown on soils amended (by volume) with 0, 20, 40, and 60% Source-Separated Municipal Solid Waste (SS-MSW) compost. Dill (*Anethum graveolens* L.) and peppermint (*Mentha X piperita* L.) were grown on soil amended with 0, 20, 40, and 60% (by volume) of high-Cu manure compost. The SS-MSW compost applications increased the concentration of Cu and Zn in all fractions, increased Mn in acid extractable (ACID), manganese oxide (FeMnOX) and OM fractions, but decreased slightly exchangeable-Mn. Addition of 60% high-Cu manure compost to the soil increased Cu Exchangeable (EXCH), ACID, FeMnOX, and OM fractions, but decreased EXCH-Mn, and did not change EXCH-Zn. Addition of both composts to soil reduced bioavailability and transfer factors for Cu and Zn. Their results suggest also that mature SS-MSW and manure composts with excess Cu and Zn could be safely used as soil conditioners for agricultural crops (Zheljazzkov and Warman 2004).

### TOXICITY OF HEAVY METALS IN SOIL APPLIED WITH COMPOST MANURE

Several studies have been reported on the study of pollutant toxicity in compost to plants (Wong 1985b; Pinamonti *et al.* 1997; Mbarki *et al.* 2008; Oleszczuk 2008) or soil microorganism (Bhattacharyya *et al.* 2005). Pinamonti *et al.* (1997) tested three organic soil conditioners in 14 different *Malus domestica* orchards; cattle manure, sewage sludge and poplar barks (SB) compost and MSW compost (from municipal solid waste not source separated). The soil conditioners differed in the metal content; MSW compost > SB compost > cattle manure. For six years, Zn, Cu, Ni, Pb and Cr content were monitored in the soil, both in total and EDTA extractable form and in leaves and fruits. SB compost did not cause significant increase in heavy metal content in soil and plants, making it suitable as fertilizer in short to medium term. On the other hand, MSW compost increased the concentrations of Zn, Cu, Ni, Pb and Cr in the soil, both in total and EDTA extractable forms. In case of Pb and Cd, increase was also observed in the vegetables and fruits. A study by Oleszczuk (2008) looked at the effects of both heavy metals and polycyclic aromatic hydrocarbons in compost onto the plants. Four municipal sewage sludges were composted for 76 days. A Phytotoxkit test and pot experiment with *Lepidium sativum* were used for the bioassay. The total PAH content in the sludges ranged from 3674.1 to 11236.3  $\mu\text{g kg}^{-1}$ . Concentration range of heavy metals were 1.9-76  $\text{mg kg}^{-1}$  for Cd, 27.6-120  $\text{mg kg}^{-1}$  for Cr, 156-335  $\text{mg kg}^{-1}$  for Cu, 37.5-59.5  $\text{mg kg}^{-1}$  for Pb, 21.7-155  $\text{mg kg}^{-1}$  for Ni and 1015-1385  $\text{mg kg}^{-1}$  for Zn. Varied sewage sludge toxicity results in relation to the plant tested were in this case obtained. In two sludges, a 100% inhibition of seed germination was noted. Sludge composting limited their negative influence on most of the phytotoxicity parameters. Contrasting effects of municipal compost on alfalfa growth in clay and in sandy soils in terms of N, P, K content and heavy metal content toxicity has been reported by Mbarki *et al.* (2008). Studies were carried out for six months in a greenhouse. Mature municipal solid waste compost (MSWC) from Tunis city was applied to clay and soil from cultivated fields at rates equivalent of 40, 80, 120  $\text{t ha}^{-1}$ . Results revealed plant growth is determined by strong interaction that exists between compost and soil nature. Plant growth yields were significantly lower in sandy soil than in clay soil and was independent of the amendments. At the end of experiment, heavy metal content in amended clay soil remained higher than in amended sandy soil which was attributed to metal adsorption on clay and organic matter and precipitation onto oxides, hydroxide and carbonates. Leaching of metals in sandy soil could have contributed to lower values.

Bhattacharyya *et al.* (2005) studied the microbial biomass and enzyme activities in submerged rice soil amended

with municipal solid compost and decomposed cow manure. Experiments were conducted during wet seasons on rice grown under submerged condition. The treatments consisted of the following: control, no input; MSW compost, at 60  $\text{kg N ha}^{-1}$ ; well decomposed cow manure (DCM), at 60  $\text{kg N ha}^{-1}$ ; MSW compost (30  $\text{kg N ha}^{-1}$ ) + Urea (30  $\text{kg N ha}^{-1}$ ); DCM (30  $\text{kg N ha}^{-1}$ ) + U (30  $\text{kg N ha}^{-1}$ ) and Fertilizer, (at 60: 30: 30 NPK  $\text{kg ha}^{-1}$  through urea, single superphosphate and muriate of potash respectively). The soil microbial biomass-C (MBC), MBC as percentage of organic-C (ratio index value, RIV), urease and acid phosphatase activities were higher in DCM than MSWC-treated soils, due to higher amount of biogenic organic materials like water soluble organic carbon, carbohydrate and mineralizable nitrogen in the former. Experiments where urea was integrated with DCM or MSWC have higher studied parameters compared to their single applications. It was observed that soil MBC, urease and acid phosphatase activities periodically declined up to 60 day after transplanting (DAT) and then increased after crop harvest. The heavy metals in MSWC did not detrimentally influence MBC, urease and acid phosphatase activities of soil but regular monitoring for soil parameters is needed in the event of long term MSWC application since heavy metals are persistent.

### CONCLUSIONS

The major components of compost materials used are sewage and wastewater sludge, municipal solid waste and saw dust. In general, heavy metals and organic contaminants are present in large concentrations in sludge followed by sawdust and least in biowaste municipal solid waste. In sludge samples, the concentration of the most common heavy metals can be given in the following decreasing order: Zn > Cu > Cr > Pb > Ni > Fe > Hg > Cd. The major sources of organic contaminants in the sludge samples is from various industrial processing plants such as steel, fuel, formulations and wood processing. Separated municipal solid waste has less contaminant than mixed one. Further, source separated MSW gives much better reduction in contaminants than centrally separated one and is therefore idea for composting. Bioavailability, fate and toxicity are influenced by several factors such as the type of metal, amount of ash, pH, humic substances and organic matter in the compost or applied soil. A linear correlation exists between metal partitioning in various fractions of the compost or applied soil and pH, humic substances, ash and organic matter.

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