Solubility and Availability of Heavy Metals in Soils as Affected by Compost Amendment

Mohamed L. Moharem[1]

ABSTRACT

The effect of agriculture solid waste compost on the availability of native and spiked Cd, Cu, Ni, and Zn in three different soils was evaluated. The three soils were spiked separately with the metals at concentration of 800 mg kg soil^{-1} and amended with three rates of the compost (0, 3, and 6 %-w/w). The mixtures of soil-compost were allowed to age at room temperature for 30 and 90 days. After each period, they were extracted for readily soluble and exchangeable (2.5% acetic acid), available (DTPA), and bound to organic matter (sodium pyrophosphate) metal species. Addition of compost generally reduced the extractability of the soluble and exchangeable forms of all native and spiked metals. This effect was directly related to the amount of added compost and increased with ageing time. The potentially plant-available Cd and Cu extracted with DTPA were generally reduced with increasing additions of compost and incubation time. There was increase of sodium pyrophosphate extractable Cd and Cu as a result of compost amendment and incubation time increase. Conversely, recovery of Zn in DTPA-extract was larger with increasing both compost and incubation period whereas Ni remained invariant with compost additions with slightly decrease in metal solubility during aging. The obtained results suggest that soil amendment with compost-organic matter may accelerate the immobilization of native and spiked heavy metals in soils due to reducing readily soluble and exchangeable all metals in addition to reducing possible plant uptake of- at least- Cd and Cu.

Keywords: Solubility, Heavy metals, Compost, Incubation time.

INTRODUCTION

Soil contamination with heavy metals is a worldwide problem. Accumulation of heavy metals in soils can adversely affect soil ecology, agricultural productivity, quality of agricultural products and water resources, human and animal health problem (Raicevic et al., 2005). Among available remediation technologies, in situ immobilization of heavy metals using a chemical amendment can be a cost-effective and environmentally sustainable remediation approach for the immobilization of heavy metals by reducing the mobility and availability. This immobilization technique may provide a long-term remediation solution if low solubility minerals and/or stable precipitates are produced in situ (Vangronsveld and Cunningham, 1998). Therefore, the choice of the soil amendments need that the amendments must reduce heavy metals transfers from contaminated soils to the surface water or groundwater and uptake by plants and organisms.

Several authors have suggested the use of residual materials such as compost for in situ remediation of heavy metal contaminated soils, as the least ecologically damaging and least expensive remediation technique (Geebelen et al., 2002 and Nwachukwu and Pulford, 2008). Compost has been reported as having a great potential for retaining trace elements in non-available forms (Smith, 2009), potentially reducing their overall bioavailability due to several processes, including raising soil pH, complexation, sorption, precipitation, or a combination of them, thus providing an effective soil remediation technique (Brown et al., 2003). However, some drawbacks may happen with this technique, namely the potential mobilization of some elements (in particular Cu) associated to dissolved organic matter (Zhou and Wong, 2001), and the re-release of the immobilized elements after organic matter mineralization in the long term. These drawbacks can in fact be avoided, first, because high loads of dissolved organic matter are expected only when low-stabilized organic materials are employed, as their concentrations decrease with compost maturity. There is no evidence that trace element availability increases with time in compost-amended soil as a result of organic matter mineralization (Smith, 2009). Therefore, employing non-stabilized organic materials for this purpose should be avoided in order to keep the potential drawbacks at a minimum. Furthermore, compost materials may contain high levels of heavy metals depending on their source and may increase their contents in amended soil depending on the ability of compost components to bind metal in addition to various soil conditions. Therefore, this study was designed (1) to assess the effect of potentially metals originating from compost on metals forms in incubated soils and (2) to study the effect of compost amendment on native metals form and (3) to evaluate the behavior of heavy metals freshly added to soils during the incubation periods and (4) to examine the effect of compost amendment on freshly added metals form.

MATERIALS AND METHODS

Soils:

Three soil samples, varying in organic matter and calcium carbonate contents, were used in this study. Sandy soil was collected from Elbostan, 80 Km south west Alexandria city and calcareous soil from El-Nahda, 40 Km south west Alexandria city. Abu-Rawash soil was collected from Abu-Rawash area of Great Cairo city with historically irrigation with primary treated wastewater from Abu-Rwash wastewater treatment plant. The soil samples were air-dried, ground, passed through a 2-mm sieve and stored in plastic bags for use. Selected chemical and physical properties of the three soils are shown in Table 1. Soil pH was measured in 1:2 soil: water suspension and electric conductivity (EC) was measured in soil paste extract (Richards, 1954). The bioavailable Cd, Cu, Zn and Ni were extracted by DTPA (Lindsay and Norvell, 1978) and measured by atomic absorption spectroscopy (contrAA 300). Organic matter content was determined by the method of Walkley and Black (Nelson and Sommers, 1982), total carbonate equivalent was determined by calcimiter method (Nelson, 1982), and cation exchange capacity was measured by the method of Rhoades (1982). Metal concentrations were determined according to the method described by Ure (1995). Particle size analysis was determined by the hydrometer method (Hillel *et al.*, 1972).

Compost:

Compost less than 5 mm derived from organic waste material mainly agriculture solid waste (ASW) were obtained from Nahdat Misr Company for Environmental services (formally was named Veolia) in Alexandria city. The analysis of the main properties of the compost was conducted as follows: pH was determined in aqueous extracts (substrate/extractant ratio: 1/5, v/v). Total organic matter (OM) was determined by Walkley and Black (Nelson and Sommers, 1982). Total N was measured by Kjeldahl digestion of samples and steam distillation (Keeney and Nelson, 1982). Total concentrations of heavy metals in aqua regia digested extract (Esakku et al. 2005) were analyzed using flame atomic absorption spectrometry (contrAA 300). The main chemical properties of the compost are shown in Table 1.

Incubation experiment:

The soils were mixed by hand with the compost at two rates: 3% and 6% (dry weight), roughly equivalent to 60 and 120 t ha^{-1}. The soils alone and the mixtures with compost were contaminated separately with a solution containing $Cu(NO_3)$, $Cd(NO_3)_2$, $Zn(NO_3)_2$ or $Ni(NO_3)_2$ in order to obtain a final concentration of 800 mg kg^{-1} (dry weight) for each element in soil. The soils were incubated for 30 or 90 days by the following treatments:

- Non-spiked soil and amended with each compost rate, to study the effect of potentially metals originating from compost on metals forms in incubated soils, and also to study the effect of compost amendment on native metals form.

- Spiked soil, to study the behavior of heavy metals freshly added to soils during the incubation periods.

- Spiked soil and amended with each compost rate, to study the effect of compost amendment on freshly metals form.

The moisture content was maintained throughout the experiment around 80% of their field capacity, replacing weight losses with distilled water. Composite samples were taken after each period and air-dried for analysis.

Soil extractants:

At the end of each incubation period, the incubated soils were extracted with the following solutions: (1) 2.5% glacial acetic acid (v/v), for readily soluble and easily exchangeable forms of metals (Alloway and Davis, 1971); (2) 0.005 M DTPA in 0.01 N $CaCl_2$ and 0.1 M triethanolamine at pH=7.3, for plant-available metals (Lindsay and Norvell, 1978); (3) sodium pyrophosphate, for metals bound to organic matter. For first and second extractants, 10 ml of solution were added to 5 g of soil sample placed in polypropylene bottles and shaken on a rotating shaker for 2 h. The suspension was then filtered and the filtrate brought to 50ml. For Pyrophosphate-extracted elements, one hundred milliliters of 0.1M Na-pyrophosphate were added to 1 g of soil and the resulting suspension was shaken for 16 h (McKeague, 1967). Five drops of 0.04% Superfloc were added to the extract before centrifugation in order to produce the flocculation of clay. The concentration of metals in the supernatant of the three extractants was measured with a flame Atomic Absorption Spectrometry (contrAA 300).

RESULTS AND DISCUSSIONS

The three soils chosen for this study differ substantially in their native OM and calcium carbonate content. The calcareous soil is characterized by high calcium carbonate content. In comparison with calcareous and sandy soils, Abu-Rawash soil showed more organic matter, higher CEC value and total content of Cu, Ni, and Zn (Table 1); considering the past irrigation with primary treated wastewater from Abu-Rwash wastewater treatment plant in the periodically area from which the Abu-Rawash soil was collected.

Table 1. The main chemical and physical properties of the studied soils and compost

Characteristics	Units	Calcareous	Sandy	Abu-Rawash	Compost
pH		7.9	8.0	6.87	7.9
EC	dS m^{-1}	4.54	1.12	2.99	4.7
Clay	%	26.8	19.4	1.3	-
Silt	%	6.4	13	3.9	-
Sand	%	66.8	67.6	94.8	-
Texture		sandy clay loam	sandy	sandy	-
OM	%	1.5	0.4	3.21	75.16
CaCO$_3$	%	26	19		-
CEC	cmol$_c$ kg^{-1}	18	5	33	52
TOC	%	0.87	0.23	1.86	43.70
N	%	-	-	-	3.13
C/N		-	-	-	14
Total metal	mg kg^{-1}				
Cu		33.48	20.58	51.34	210.25
Cd		0.01	0.05	-	-
Zn		25.66	21.22	132	844.88
Ni		2.1	2.5	14.79	4.32
DTPA-extractable metal	mg kg^{-1}				
Cu		5.21	3.56	5.23	-
Cd		-	-	-	-
Zn		1.33	0.63	12.34	-
Ni		-	-	2.12	

EC: Electrical conductivity; OM: Organic matter; CEC: Cation exchange capacity; TOC: Total organic carbon; C/N: carbon : nitrogen ratio

The amount of soluble and exchangeable heavy metals recovered by extraction with 2.5% acetic acid in the three soils after two incubation periods are reported in Tables 2 and 3. The compost additions to soils which were not spiked with heavy metals were studied only for Abu-Rawash soil due to high content of native heavy metals comparing with the other two soils. However, native Cd of Abu-Rawash soil was not studied due to the non detected measurement of this metal in both soil and compost. As shown in Table 2, the solubility in acetic acid of the original heavy metals for the un-spiked Abu-Rawash soil produced a general decrease of the concentrasion of the acetic acid-extractable metals as a result of compost addition to soil with more pronounced at high addition level. This effect was noticeable for the original content of all metals after both 30 and 90 days of incubation.

Following three soils individually enrichment with heavy metals, the quantity of metals recovered in 2.5% acetic acid for control samples (no compost addition) was significantly lower than the amount added to three soils (Table 3), thereby indicating that ageing processes control the extractability of heavy metals in soils. However, control soils showed a different ageing effect with diverse metals. While the solubility in acetic acid significantly decreased with incubation for all metals in the OM-rich Abu-Rawash soil or calcium carbonate-rich calcareous soil, that of Cd and Zn did not

significantly change in the period between 30 and 90 days for the OM and calcium carbonate-poor sandy soil. This suggests a role of the native OM or calcium carbonate of both soils in progressively increasing the retention of soluble and exchangeable heavy metals. The larger amount of native OM in the Abu-Rawash soil is capable to strongly complex all added metals which become less soluble in acetic acid, whereas the lower OM content in the sandy soil may have not been reactive enough to stabilize the weaker complexes with Cd and Zn (Stevenson and Ardakani, 1972; Stevenson, 1977). Furthermore, the high contents of CaCO$_3$ in calcareous soil could be responsible for the high metals retention through incubation period of this soil (Ponizovsky et al., 2007; Basta et al., 2001; Mcbride, 1994).

The soils treated with increasing amounts of compost had the general effect of gradually reducing the solubility of heavy metals in acetic acid in respect to control(Table 3). Furthermore, incubation time generally reduced further the metals extractability, though differences between the three soils were noticed. For instance, Cu availability in sandy soil was decreased from 71 to 42 mg kg^{-1} after 30 day incubation time as a result of adding high compost level.

Table 2. The amount of 2.5% acetic acid, DTPA, sodium pyrophosphate extractable native metals (mg kg^{-1}) of compost amended Abu-Rawash soil after the 30 and 90 days of incubation

		Ac			DTPA			Pyr		
		\% Added compost (w/w)								
		0	3	6	0	3	6	0	3	6
Cu	30 d	6aA	4aB	2.4aC	2aA	1.3aA	0.97aB	10aC	12aB	14aA
	90 d	4.8bA	3bB	1bC	1.6aA	1aA	0.67bB	11aC	14.2bB	17.5bA
Zn	30 d	4aA	3aB	2.5aC	4aC	5.9bB	7bA	7aA	7.2aA	6.8aA
	90 d	3.51bA	2.41bB	1.91bC	4.8aC	8aB	10aA	6.8aA	6.89aA	6.4aA
Ni	30 d	3aA	2.8aA	2.1aB	2.34aA	1.95aA	1.6aA	8.32aA	8.51aA	7.97aA
	90 d	2.4aA	1.8bB	0.67bC	1.75bA	1.67aA	1.1aA	8.14aA	7.99aA	7.83aA

Ac, acetic acid; Pyr, sodium pyrophosphate.
All values are average of three replications. Means within a (vertical) column for both incubation time followed by the same lower case letter do not differ significantly by the Duncan's multiple range test (p< 0.05). Means within a (horizontal) row for a given level of % compost addition followed by same capital case letter do not differ significantly by Duncan's multiple range test (p< 0.05)

Table 3. The amount of 2.5% acetic acid extractable spiked metals (mg kg^{-1}) of the compost amended three soils after the 30 and 90 days of incubation

		Calcareous			Sandy			Abu-Rawash		
		\% Added compost (w/w)								
		0	3	6	0	3	6	0	3	6
Cd	30 d	46aA	40aB	32aC	198aA	172aB	108aC	292aA	242aB	186aC
	90 d	42.5bA	33.5bB	26bC	196aA	150bB	80bC	196bA	140.5bB	96.43bC
Cu	30 d	14aA	13aB	11aC	71aA	50aB	42aC	198aA	166aB	116aC
	90 d	13bA	11.1bB	8bC	60.34bA	40.43bB	29.5bC	178.5bA	144.5bB	96bC
Zn	30 d	250aA	238aB	220aC	363aA	359aB	309aC	433aA	420aB	411.76aC
	90 d	237b	234.5b	200b	360.5bA	351bB	242.5bC	397bA	340bB	328.5bC
Ni	30 d	36aA	20aB	14aC	73aA	58aB	46aC	161aA	154aB	142aC
	90 d	25.5bA	17bB	9bC	52.5bA	44bB	30bC	120bA	119bA	104bB

All values are average of three replications. Means within a (vertical) column for both incubation time followed by the same lower case letter do not differ significantly by the Duncan's multiple range test (p< 0.05). Means within a (horizontal) row for a given level of % compost addition followed by same capital case letter do not differ significantly by Duncan's multiple range test (p< 0.05).

Moreover, after the second incubation period of this soil, additional reduction of Cu concentration was obtained reaching 29.5 mg kg^{-1}. These findings suggest that compost amendments contribute strongly to reduce the solubility of heavy metals and presumably also their mobility in the soil solution.

DTPA solution is commonly used to estimate plant-available metals (Lindsay and Norvell, 1978). This extractant can also evaluate the fraction of metals complexed by OM (Piccolo and Celano, 1992). The additions of compost to Abu-Rawash soil which were not spiked with heavy metals showed a decrease in DTPA-extractable native Cu, and this effect was increasing during metals aging by the compost amendment. In contrast, incubation time and compost amendment showed an increase of Zn solubility in DTPA extract whereas Ni recovery was not significantly affected by both incubation time and compost amendments (Table 2). The effect of compost on the availability of native metals in this soil can be referred to metal content/form in both soil and compost. High content of Cu and Zn is seen in both compost and Abu-Rawash soil (Table 1). Thus, the increase of Zn recovery due to compost amendment in contrast to what

was noticed for Cu may be attributed to the difference in the chemical form of both metals in soil and compost.

Copper and zinc showed a different ability towards compost components. For example, He *et al.* (1995) showed that > 50– 80% of Zn was extracted in a relatively labile organic fraction from municipal solid waste-composts. Copper, on the other hand, was bound to more humified organic matter (approximately 50%) and was therefore considered to be relatively immobile. Thus, in the current study, the increase of DTPA extractable Zn as an increase of compost rate could be related to low ability of compost constituents for Zn retention leading to easily release of compost native Zn once increase of amendment rate. On the other hand, the high stability of Cu hold in compost matrix as discussed could be responsible for the low extractability of Cu in DTPA extract.

Values of metals in DTPA extraction from the three spiked soils are shown in Table 4. The DTPA solution was capable to extract significantly larger amount of metals than that of the acetic acid. The progressive increase of the compost additions decreased Cd and Cu solubility in DTPA. Further decrease in DTPA extractable Cd and Cu was obtained when incubation time passed from 30 to 90 day for the three soils. The highest stability constants for Cu in humic complexes (Schnitzer and Skinner, 1967; Stevenson, 1977) and the tendency of Cd to preferably associate with larger, humified, and less soluble organic materials (Kaschl *et al.*, 2002) may account for the reduced availability of Cu and Cd with incubation time due to OM-rich compost amendment. These results indicate the role of

organic matter originated from compost amended soils on reducing metals availability. This is in line with the findings of other researchers in the direction that compost inputs to contaminated soils containing large fractions of labile elements reduce their overall bioavailability (Smith, 2009 and Brown *et al.*, 2003).

In contrast to what was generally observed for Cd and Cu; Zn and Ni behaved a contrast trend. The mean values of Ni recovered in DTPA were the lowest for all added metals and remained invariant with compost additions in the soils after each incubation period with slightly decrease in metal solubility during aging. Conversely, in the three soils the mean values of Zn were enhanced with the increase of both compost amendments and incubation time with respect to control. The low solubility of Ni in DTPA extract comparing with the other metals in addition to its independent behavior toward compost addition indicated the low ability of Ni toward organic matter since DTPA extractant can also solubilize metals chelated with organics (Piccolo and Celano, 1992). This result is in line with Schnitzer and Skinner (1967) who observed the low value of stability constant of this metal in complexes with humic matter. However, the slight decrease of DTPA-Ni with incubation time by the compost amendment may be due to the predominance of mineral species for Ni (Halim et al., 2003). It was reported that Ni can be strongly retained in soils as precipitates which may be considered an irreversible form on soils and minerals (Voegelin and Kretzschmar, 2005).

Table 4. DTPA extractable spiked metals (mg kg^{-1}) of the compost amended three soils after the 30 and 90 days of incubation

		Calcareous			Sandy			Abu-Rawash		
		% Added compost (w/w)								
		0	3	6	0	3	6	0	3	6
Cd	30 d	430aA	412aB	392aC	614aA	528aB	464aC	606aA	574aB	504aC
	90 d	375.5bA	347.5bB	315bC	598bA	498bB	405.5bC	487.5bA	429.5bB	363bC
Cu	30 d	295aA	284aB	200aC	427aA	391aB	390aB	406aA	391aB	340aC
	90 d	271.5bA	239bB	176bC	415.5bA	354bB	339.5bC	290.5bA	253.5bB	220bC
Zn	30 d	342aC	345bB	360bA	395aC	436bB	473bA	379aC	387.3bB	402bA
	90 d	329bC	350aB	374aA	378bC	443aB	490aA	358.5bC	398aB	443.5aA
Ni	30 d	99aA	98aA	98.6aA	76aB	77aA	78aA	88aA	87.2aA	87.1aA
	90 d	94.5bA	95bA	94.1bA	70.5bA	71.3bA	69.2bA	86bA	85bA	84.8bB

All values are average of three replications. Means within a (vertical) column for both incubation time followed by the same lower case letter do not differ significantly by the Duncan's multiple range test (p< 0.05). Means within a (horizontal) row for a given level of % compost addition followed by same capital case letter do not differ significantly by Duncan's multiple range test (p< 0.05).

Table 5. Sodium pyrophosphate extractable spiked metals (mg kg^{-1}) of the compost amended three soils after the 30 and 90 days of incubation

		Calcareous			Sandy			Abu-Rawash		
		% Added compost (w/w)								
		0	**3**	**6**	**0**	**3**	**6**	**0**	**3**	**6**
Cd	30 d	208bC	221bB	247bA	60.32aC	77.32bB	85.12bA	330.5bC	369.3bB	403.5bA
	90 d	213aC	231aB	275aA	61.32aC	85.43aB	96.5aA	336.32aC	379aB	430aA
Cu	30 d	220bC	263bB	277bA	66.1aC	78bB	90bA	390bC	432bB	442bA
	90 d	228aC	286aB	320aA	67.5aC	89aB	121aA	392aC	461aB	565aA
Zn	30 d	11aA	12aA	10aA	7.32aA	7.9aA	7.8aA	12.32aA	11.9aA	11.3aA
	90 d	11.2bA	10bA	8bB	7.3aA	7.1bA	7bA	11.8aA	10.5bA	9.45bB
Ni	30 d	13.2aA	12.8aA	12.5aA	8.32aA	8.11aA	7.9aA	13.2aA	13.9aA	12.9aA
	90 d	12.5aA	11.7bA	11.4bA	8.1aA	7.9aA	7bB	12.8bA	12.7bA	11.9bB

All values are average of three replications. Means within a (vertical) column for both incubation time followed by the same lower case letter do not differ significantly by the Duncan's multiple range test (p< 0.05). Means within a (horizontal) row for a given level of % compost addition followed by same capital case letter do not differ significantly by Duncan's multiple range test (p< 0.05).

The contrast response between Cd, Cu and Zn toward compost may be referred to the different affinity of these metals to complex with organic matter. Several researchers showed the potential of compost as sorbent for Cu and Cd rather than Zn (Grimes *et al.*, 1999; Song and Greenway, 2004), suggesting that humic substances were likely to be the main sites of metal sorption. Additionally, McBride (1994) reported that Zn is less strongly sorbed to organic matter than Cu; and this is due to the stronger binding sites for Cu by virtue of its lower electronegativity and higher charge to radius ratio, and also to the higher affinity of Zn for iron oxides.

Values for metals recovered by sodium pyrophosphate extraction after 30 and 90 d of incubation for native and freshly added metals are shown in Tables 2 and 5. This extractant is commonly used to estimate the pool of elements associated to organic matter (Paradelo *et al.*, 2011). For Cd and Cu, in general, both native and spiked metals were increased in the organic fraction as a result of compost amendments. The increase of incubation time of the three soils from 30 to 90 days in the presence of compost caused additional increase of both metals in sodium pyrophosphate extract with more intense at the highest rate of compost. For instance, at high compost amendment rate in sandy soil, Cu produced increasing in that fraction linked to organic matter, comparing with control, reaching almost a 36 and 79% at the end of the first and second incubation period, respectively. This result validates the hypotheses that metals sorption process onto organic matter may be responsible for increasing metal retention in compost amended soils. In contrary, Zn and Ni illustrated an independent behavior toward organic matter since in most cases both metals were not significantly changed with compost additions in the soils after each incubation period. Moreover, Ageing of Zn and Ni in soils reduces even its solubility in sodium pyrophosphate, reflecting a poor incorporation of both metals into organic matter.

CONCLUSIONS

The present study indicates that the potential environmental availability of native and freshly added metals to soils may be controlled by soil amendment with compost substance. The availability of metals, for both native and freshly added, in the 2.5% acetic acid extraction was generally reduced with compost amendment. This suggests that the ''passive'' physical mobility of metal species in soils (diffusion, mass transport) and the consequent risk of lateral and vertical contamination of water bodies may be effectively reduced with addition of reactive compost amendment. The potential availability of native and spiked Cd and Cu to plant uptake, an ''active'' process carried-out by root-exuded organic acids, that is mimicked by the well-established soil extraction with DTPA, generally diminished in soil amended with compost addition.

Also, ageing of metals in samples magnifies the effect of compost amendment in the three soils. In contrary, the predominance of Ni and Zn to mineral species rather than organic matter may be responsible for the independent response of Ni to DTPA extraction and the increase of DTPA extractable Zn due to compost amendment. The fraction associated with organic matter (pyrophosphate-extractable) confirms that the mechanism of availability reduction by compost amendment was probably the association of Cu and Cd with organic matter.

These results showed that – at least for Cd and Cu – the amendment of metal-contaminated soils with compost could be an effective method for soil remediation due to the reduction of the mobility and availability of potentially toxic elements. Another advantage of using compost is suggesting that, at least at the rates employed here, the compost will not act as a source of contaminants even in case of Zn that while compost amendment is potentially useful to increase plant-availability of Zn in soil suffering from precipitation problem, they concomitantly reduce the environmental mobility and migration of this metal far from rhizosphere. The current results appear encouraging for an experimental upscale that verifies the role of compost in reducing plant uptake of heavy metals in soils contaminated with toxic metals.

REFERENCES

Alloway, B.S. and B.E. Davis. 1971. Trace element content of soils affected by base mining in Wales. Geoderma 5: 197-207.

Basta, N.T., R. Gradwohl, K.L. Snethen, and J.L. Schorden. 2001. Chemical immobilization of lead, zinc and cadmium in smelter contaminated soils using biosolids and rock phosphate. J. Environ. Qual. 30: 1222-1230.

Brown, S.L., C.L. Henry, R. Chaney, H. Compton, and P.S. DeVolder. 2003. Using municipal biosolids in combination with other residuals to restore metal-contaminated mining areas. Plant Soil 249: 203-215.

Esakku, S., A. Selvam, J. Kurian, K. Palanivelu .2005. Assessment of heavy metal species in decomposed municipal solid waste. Chem. Spec. Bioavailab. 17:95-102.

Geebelen, W., J. Vangronsveld, D.C. Adriano, R. Carleer, and H. Clijsters. 2002. Amendment induced immobilization of lead in a lead-spiked soil: Evidence from phytotoxicity studies. Water Air Soil Pollut. 140: 261-277.

Grimes, S.M., G.H. Taylor, and J. Cooper. 1999. The availability and binding of heavy metals in compost derived from household waste. J. Chem. Technol. And Biotechnol. 74:1125-130.

Halim, M., P. Conte, and A. Piccolo. 2003. Potential availability of heavy metals to phytoextraction from contaminated soils induced by exogenous humic substances. Chemosphere 52: 265-275.

He, X.T., T.J. Logan, and S.J. Traina. 1995. Physical and chemical characteristics of selected U.S. municipal solid waste composts. J. Environ. Qual. 24:543-52.

Hillel, D., V.D. Krentos, and Y. Stylianov. 1972. Procedure and test of an internal drainage method for measuring soil hydraulic characteristic in situ. Soil Sci. 114:395-400.

Kaschl, A., V. Romheld, and Y. Chen. 2002. Cadmium Binding by Fractions of Dissolved Organic Matter and Humic Substances. J. Environ. Qual. 31:1885-1892.

Keeney, D.R. and D.W. Nelson. 1982. Nitrogen-inorganic forms, in: A.L. Page (Ed.), Methods of Soil Analysis. Part 2. Chemical and microbiological properties, Am. Soc. Agron., Madison, pp. 643–698.

Lindsay, W.L. and W.A Norvell,. 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci. Soc. Amer. J. 42:421-428.

McBride, M. B. 1994. Environmental Chemistry of Soils. Oxford University Press, New York.

McKeague, J.A. 1967. An evaluation of 0.1M pyrophosphate-dithionite in comparison with oxalate as extractants of the accumulation products in podzols and some other soils. Can. J. Soil Sci. 46: 13-22.

Nelson, D.W. and L.E. Sommers. 1982. Total carbon, organic carbon and organic matter. In: Page AL, Miller RH, Keeney DR (eds) Methods of Soil Analysis. Am. Soc. Of Agron., Madison,Wisconsin, USA, pp 539–549.

Nelson, R.E. 1982. Carbonate and gypsum. In: Page AL, Miller RH, Keeney DR (eds) Methods of Soil Analysis. Amer. Soc. Agron. , Madison, pp 181-197.

Nwachukwu, O.I. and I.D. Pulford. 2008. Comparative effectiveness of selected adsorbant materials as potential amendments for the remediation of lead, copper and zinc-contaminated soil. Soil Use Manage. 24: 199-207.

Paradelo, R., A. Villada, A.R. Devesa-Rey, A.B. Moldes, M. Domínguez, J. Pati~no, and M.T. Barral. 2011. Distribution and bioavailability of trace elements in municipal solid waste composts. J. Environ. Monitor. 13: 201-211.

Piccolo, A. and G. Celano. 1992. Distribution of heavy metals in profiles of a hydromorphic soil system. Fres. Environ. Bull. 1: 16-21.

Ponizovsky, A., H.E. Allen, and A.J. Ackerman. 2007. Copper activity in soil solutions of calcareous soils. Environ. Pollut. 145: 1-6.

Raicevic, S., T. Kaludjerovic-Radoicic, and A.I. Zouboulis. 2005. In situ stabilization of toxic metals in polluted soils using phosphates: Theoretical prediction and experiment verification. J. Hazard. Mater. 117: 41-53.

Rhoades, J. D. 1982. Cation exchange capacity. In: A.L. Page (ed.) Methods of Soil Analysis. Part 2: Chemical and microbiological properties (2nd ed.) Agronomy 9:149-157.

Richards, L.A. 1954. Dignosis and improvement of alkaline soils. USDA Handbook 60. US Government Printing Office, Washington, DC, USA, p 152.

Scheidegger, A.M., D.G. Strawn, G.M. Lamble, and D.L. Sparks. 1998. The kinetics of mixed Ni-Al hydroxide formation on clay and aluminum oxide minerals: A time-resolved XAFS study. Geochim. Cosmochim. Ac. 62:2233-2245.

Schnitzer, M. and S.I.M. Skinner. 1967. Organo-metallic interactions in soils: Stability constants of Pb, Ni, Co, Ca and Mg–fulvic acid complexes. Soil Sci. 103: 247- 252.

Smith, S.R. 2009. A critical review of the bioavailability and impacts of heavy metals in municipal solid waste composts compared to sewage sludge. Environ. Int. 35: 142-156.

Song, Q.J. and G.M. Greenway. 2004. A study of the elemental leachability of and retention capability of composts. J. Environ. Monitoring 6:31-37.

Stevenson, F.J. 1977. Nature of divalent transition metal complexes of humic acids revealed by modified potentiometric titration method. Soil Sci. 103: 10-17.

Stevenson, F.J. and M.S. Ardakani. 1972. Organic matter reactions involving micronutrients in soils. In: Mortvedt, J.J. (Ed.), Micronutrients in Agriculture. American Society of Agronomy, Madison.

Ure, A.M. 1995. Methods of soil analysis for heavy metals in soils. In: Alloway BJ (ed) Heavy metals in soils, 2nd edn. Blackie Academic and Professional, London, pp 58–95.

Vangronsveld, J. and S.D. Cunningham. 1998. Introduction to the Concepts. Metal-Contaminated Soils: In-Situ Inactivation and Phytorestoration. Pp: 1-15.

Voegelin, A. and R. Kretzschmar. 2005. Formation and dissolution of single and mixed Zn and Ni precipitates in soil: Evidence from column experiments and extended X-ray absorption fine structure spectroscopy. Environ. Sci. Technol. 39:5311-5318.

Zhou, L.X. and J.W.C. Wong. 2001. Effect of dissolved organic matter from sludge and sludge compost on soil copper sorption. J. Environ. Qual. 30: 878-883.

–

.   –

.

DTPA

.(   )   /

(%   )
(   )   (   )

.

.

DTPA

.   DTPA

.

)

(

.

.