

Competitive Adsorption of Cu, Zn and Mn on Compost Amended Soils with Variable Clay Content

M. S. Kotb

Department of Soils & Water, Faculty of Agriculture, Cairo University, Egypt.

THE AIM of this study was to assess the effects of a single application of compost derived from crop wastes, and incubated for 60 days, on the competitive adsorption of Cu, Zn and Mn on four soil samples with different clay contents (2%, 10%, 20% and 40%, hereafter referred to S₂, S₁₀, S₂₀ and S₄₀) in terms of their physical and chemical properties. The competitive sorption isotherms of copper (Cu), zinc (Zn) and manganese (Mn) in multi-metal batch experiments were characterized using linear, Freundlich and Langmuir equations. All soils showed greater sorption capacity and binding strength for Cu than the other trace elements. On the basis of distribution (partition) coefficient (K_d) values for the metal concentration and maximum sorption capacity (Q) for each soil and trace element, the selectivity sequence was obtained. The greatest adsorption sequence found was Cu>Zn>Mn. Cu was the trace element most strongly adsorbed by all soils, whereas Zn and Mn were the least adsorbed in the competitive situation. The relationships between maximum adsorption and partitioning coefficients of Cu, Zn and Mn and clay content were quantitatively modeled.

Keywords: Compost, Clay, CEC, Competitive adsorption isotherm, Trace elements.

Metal adsorption to soil after the application of organic wastes has been studied in single metal systems (Illera *et al.*, 2000 and Zhou & Wong, 2001). On the other hand, few studies have investigated the competitive metal adsorption in terms of the quality of organic matter (OM) in soils amended with sewage sludge or composted sewage sludge, with naturally occurring metal concentrations. Moreover, the research efforts have focused on the evaluation of heavy metal mobility, partitioning and sorption in temperate soils (Walter *et al.*, 2002). Relatively few experiments have been conducted in inter-tropical soils (Appel and Ma, 2002).

Heavy metal adsorption and hence their plant availability do not only depend on soil constituents (inorganic and organic), but also on the nature of metals involved, and on their competition for soil sorption sites. Usually when competitive sorption of metals is compared with their monometal behavior, it is found that their adsorption is lower in the competitive systems (Harter, 1992). More strongly sorbed metals, such as lead and copper, are less affected by competition than mobile metals, such as cadmium and zinc (Zhu and Alva, 1993). However, the effect of competition among poorly sorbed metals, such as Cd, Ni, and Zn, especially in organic amended soils, has not been documented

(Chorom *et al.*, 2013). Moreover, it is not clear how the competitive adsorption of poorly sorbed heavy metals affects their behavior and availability over time.

The term adsorption is used to describe the removal of metals in solution by the solids phases (Hooda and Alloway, 1994) and includes any retention mechanism that controls availability and mobility (Serrano *et al.*, 2005). The distribution coefficient (K_d), is the capacity of the soil to resist a change of the soil solution concentration following an output of solute from (or an input of solute into) the soil (Barber, 1995). The distribution coefficient can be related to both plant uptake and environmental pollution. The mobility and fate of metals in the soil environment are directly related to their partitioning between soil and soil solution (Evans, 1989). Alloway (1995) stated that K_d is a useful parameter for comparing the sorptive capacities of different soils or materials for any particular ion, when measured under the same experimental conditions. Distribution coefficients have previously been used in studies of mobility and retention of trace elements in the soils (Martin-Garin *et al.*, 2002).

The objective of this work was to examine the impact of a single application of compost on the physical and chemical properties in four soils differing in clay content (2, 10, 20 and 40% clay), and study the sorption of Cu, Zn and Mn by sorption isotherms, to describe the competitive behavior during metal sorption in soils amended with composted and incubated for 60 days.

Materials and Methods

Four soils with different clay contents (2%, 10%, 20% and 40%, referred to S₂, S₁₀, S₂₀ and S₄₀, respectively) were collected from 0-30cm depth, the soil properties are presented in Table 1. The field capacity for all soils was determined from the soil characteristic curve using ceramic plates as described by Ryan *et al.* (2001a). The four soils were incubated with compost (crop manure compost), as their initial characteristics are shown in Table 2. The incubation experiment depended on mixing 5% of compost with soil in closed plastic vials almost as described by Mulvaney *et al.* (2001). The moisture content was maintained by weight by adding water every 4 days. At the same time samples taken for the extractions, a sufficient weight of soil was taken in crucible and kept for 2hr at 110°C in oven, to determine the moisture content of soil, so all nutrient concentration was expressed on the oven dry weight basis (Chaturvedi and Sankar, 2004).

TABLE 1. Some characteristics of soils before and after incubation period.

Soils	Clay %	pH (1:2.5)	EC dS/m	CEC Cmol/kg	TOC %	pH (1:2.5)	EC dS/m	CEC Cmol/kg	TOC %
	Before incubation					After incubation for 60 days			
S ₂	2.0	7.89	0.3	3.5	0.05	7.1	0.5	4.5	0.06
S ₁₀	10.2	7.81	0.5	16.5	0.5	7.3	2.1	20.5	0.6
S ₂₀	20.5	7.93	0.7	25.0	1.2	7.4	3.2	30.2	1.5
S ₄₀	40.2	7.71	0.8	40.5	1.5	7.3	3.1	45.5	1.8

CEC: Cation exchange capacity; TOC: Total organic carbon.

TABLE 2. Some physical and chemical properties of compost.

Crop manure compost	pH (1:10)	EC dS/m	CEC Cmol/kg	TOC %
	6.5	1.5	90	20.5

Analytical methods

Soil particle size was determined by the hydrometer method (Ashworth *et al.*, 2001). Soil pH and EC were determined in a 1:2.5 soil/water extract (Melero *et al.*, 2007) pH and EC was measured as described by Ryan *et al.* (2001b). Cation exchange capacity was determined with sodium acetate and ammonium acetate for Na extraction (Rhoades, 1982). Total organic C was measured using Walkley-Black (1934) method as described by Nelson and Sommers (1982).

Competitive sorption measurements by duplicate soil samples of 1.0g were shaken for 48 hr in polypropylene centrifuge tubes at room temperature with 50 ml of a mixed solution containing concentrations of 0, 10, 20, 30, 40, 50, 100 and 200 mg L⁻¹ of nitrate salts of Cu, Zn and Mn in a background of 0.01 M NaNO₃. Then the tubes were centrifuged at 2500 rpm for 20 min and the metal concentration in the supernatant solution was analyzed by atomic absorption spectrophotometer (AAS). Knowing the amount of metal added to the soil sample and the concentration remained in each supernatant solution, the amount of adsorbed metal could be calculated. The adsorbed amount of Cu, Zn and Mn ions onto soils was calculated as:

$$A_i = (C_i - C_e) V / M$$

where C_i and C_e are initial and equilibrium Cu and/or Zn, Mn concentrations (mM), respectively, A_i is the amount of adsorbed metal (mmole kg⁻¹), V is the solution volume (ml) and M is the weight of soil (kg). The Cu, Zn and Mn adsorption data were then fitted to the Langmuir and the Freundlich isotherms. Sorption isotherm parameters were obtained by the least square analysis using the Langmuir and Freundlich isotherms. The linear form of the Langmuir and the Freundlich isotherms are as follows:

$$C_e/C_s = 1/bQ + C_e/Q$$

$$\text{Log } C_s = 1/n \text{ Log } C_e + \text{Log } K_d$$

where: C_e =equilibrium solution phase concentration (mmol L⁻¹), C_s =equilibrium solid phase concentration (mmol kg⁻¹), Q =Langmuir isotherm sorption capacity (mmol kg⁻¹), b =enthalpy related sorption constant (L mmol⁻¹), n =sorption intensity constant (g/l) and K_d = distribution (partition) coefficient (L kg⁻¹) (Sparks, 2003).

High values of coefficient of determination (R^2) and low values of standard errors of estimate (SE) were considered as the criteria for the goodness of fits (Ghasemi-Fasaei and Bahraminia, 2013).

Results and Discussion

Incubation effects on the soil characteristics

As can be seen in Table 2, the crop manure compost has the low pH, low salinity and is high in TOC and CEC. Therefore, adding the compost to soil led to increase of the soil OM and slight change in the soil pH (Table 1). Addition of compost amendment affects the properties of soils. The treatments of the soils with compost manure resulted in decreased pH in all treatments from pH 7.89 to 7.1 in S_2 , from 7.81 to 7.3 in S_{10} , from 7.93 to 7.4 in S_{20} and from 7.71 to 7.3 in S_{40} after 60 days of incubation. The soil pH decreased in all treatments over time, which can be due to production of organic acids (Rashad *et al.*, 2011).

Compost addition resulted in an approximately twofold increase in EC in all soils. On day 60, the EC in the compost-amended soil ranged from 0.5 to 3.2 dS m^{-1} compared to 0.3 to 1.8 dS m^{-1} in the unamended soil (Table 1). Soil EC significantly increased after the addition of composts due to the presence of salts in the compost, (Table 1). Larney *et al.* (2008) also found increased EC after compost application, whereas Rashad *et al.* (2011) found that soil EC significantly declined after compost application. They explained this by an increase in salt leaching into the deeper soil layers as a result of improved aggregate stability after compost application.

The CEC was higher in S_{40} than in the other all soils and was increased by compost application by 12-28% $Cmol/kg^{-1}$. The increase in soil CEC by compost addition can be explained by the slightly increased TOC as organic matter will affect CEC by the following mechanisms: (1) more binding sites from organic matter particularly because the highly decomposed organic matter in compost has a large number of cation binding sites and (2) increasing microbial activity and therefore stimulation of decomposition of native organic matter which also increases the number of binding sites (Benito *et al.*, 2003 and Abdel-Rahman, 2009).

Effect of compost treatment on the competitive adsorption of Cu, Zn and Mn

The adsorption isotherm parameters were determined for Cu, Zn and Mn using the Freundlich and Langmuir isotherm equations of the adsorption data (Tables 3-6). Moreover, the values of the square of the correlation coefficient were reported to indicate the goodness of the model fitness.

Coefficients of determination (R^2) and standard errors of estimate (SE) for the Langmuir and the Freundlich isotherms are given in Tables 3-6. The Cu, Zn and Mn adsorption experimental data soils in multi-system well fitted to the Langmuir isotherm (Tables 3 & 4). The experimental data were also conformed

to the Freundlich isotherm (Tables 5 & 6). The evaluation of the goodness of fit demonstrated that the fit of experimental data to the Langmuir was better than the Freundlich isotherm as evidenced by relatively higher values of R^2 and lower values of SE (Tables 3-6). Ucer *et al.* (2006) observed that the adsorption data for different metals including Cu and Zn onto tannic acid immobilised activated carbon were correlated to the Langmuir and the Freundlich isotherms and the data fitted better to the Langmuir isotherm model. Ostroskia *et al.* (2009) reported that Zn dynamic isotherm onto zeolite was successfully modeled by both the Freundlich equation and the Langmuir kinetic model.

TABLE 3. Calculated Langmuir parameters of the adsorption isotherm of the investigated heavy metals by the studied soils without compost.

Elements	Q (mmol/kg)	b (L/mmol)	R ²	SE
S_{40}				
Cu	6.7	15.08	0.99	1.2
Zn	3.73	12.47	0.99	1.9
Mn	2.53	10.49	0.99	1.8
S_{20}				
Cu	6.37	11.14	0.99	0.48
Zn	2.23	8.91	0.99	1.5
Mn	1.03	8.13	0.99	1.4
S_{10}				
Cu	3.27	8.68	0.96	0.72
Zn	2.89	4.62	0.99	0.02
Mn	0.79	4.14	0.99	0.46
S_2				
Cu	2.05	1.51	0.94	0.61
Zn	0.57	1.14	0.93	0.05
Mn	0.34	1.02	0.99	0.03

TABLE 4. Calculated Langmuir parameters of the adsorption isotherm of the investigated heavy metals by the studied soils with compost.

Elements	Q (mmol/kg)	b (L/mmol)	R ²	SE
S ₄₀				
Cu	19.60	25.45	0.99	1.1
Zn	18.69	18.45	0.99	2.7
Mn	8.59	14.73	0.99	0.86
S ₂₀				
Cu	12.8	19.53	0.99	0.33
Zn	11.5	12.63	0.99	1.6
Mn	6.02	9.23	0.99	0.15
S ₁₀				
Cu	7.73	9.24	0.99	0.63
Zn	7.57	7.91	0.95	1.01
Mn	3.88	5.95	0.97	0.13
S ₂				
Cu	5.84	2.13	0.99	2.1
Zn	5.68	1.62	0.98	2.1
Mn	3.59	1.27	0.98	1.3

TABLE 5. Calculated Freundlich parameters of the adsorption isotherm of the investigated heavy metals by the studied soils without compost.

Elements	K _d (L/kg)	n (g/l)	R ²	SE
S ₄₀				
Cu	12.10	3.23	0.98	1.2
Zn	9.12	2.6	0.90	0.47
Mn	6.9	2.5	0.93	0.13
S ₂₀				
Cu	9.2	3.4	0.98	0.78
Zn	6.3	2.6	0.96	0.28
Mn	3.7	1.7	0.95	0.17
S ₁₀				
Cu	5.9	3.24	0.91	0.46
Zn	3.2	2.6	0.81	0.16
Mn	1.7	1.6	0.90	0.05
S ₂				
Cu	0.87	2.2	0.99	0.08
Zn	0.46	1.8	0.99	0.004
Mn	0.24	1.3	0.99	0.01

TABLE 6. Calculated Freundlich parameters of the adsorption isotherm of the investigated heavy metals by the studied soils with compost.

Elements	K_d (L/kg)	n (g/l)	R^2	SE
S_{40}				
Cu	24.8	3.9	0.70	3.4
Zn	17.23	3.8	0.77	2.0
Mn	12.3	3.5	0.75	0.8
S_{20}				
Cu	17.7	3.28	0.85	2.5
Zn	10.68	3.15	0.90	1.3
Mn	6.97	3.10	0.87	0.6
S_{10}				
Cu	14.0	2.6	0.91	2.2
Zn	7.0	2.5	0.81	0.8
Mn	4.21	2.4	0.90	0.3
S_2				
Cu	1.6	3.5	0.99	0.2
Zn	1.3	3.4	0.97	0.12
Mn	0.91	3.3	0.96	0.06

The results indicated that the adsorption data of Cu, Zn and Mn were generally well correlated with Langmuir and Freundlich models. Jalali and Moradi (2013) found that the Freundlich equation adequately described heavy metals adsorption. On the basis of Freundlich distribution coefficient, the selectivity sequence of the metal adsorption was $Cu > Pb > Cd > Zn > Ni > Mn$. Therefore, the maximum adsorption (Q), from the Langmuir equation, may be useful in comparing the potential adsorption capacity for the studied soils. Langmuir sorption parameters of the studied soils showed differences among the studied heavy metals, as they were reflected by their sorption maxima (Q) and bonding energy coefficient (b) (Tables 3 & 4).

Figures 1 & 2 illustrate the adsorption isotherms for Cu, Zn and Mn by the investigated soils with and without compost. Sorption isotherms for these metals by the soils exhibited differences in shape and in the amount retained. The greater competitive ability of Cu for adsorption on soil with and without compost was substantial at all metal concentrations. The copper sorption isotherm followed a trend for increasing sorption across the whole range of initial metal concentrations used. At higher metal concentrations, Cu showed the most sorption sites on the investigated soils. Sorption of Zn and Mn on soils was restricted by Cu competition. In the whole range of studied metal concentrations, Mn occupied the least sorption sites. Thus at high metal

concentrations, effects of competition were strong (Basta & Tabatabai, 1992 and Gomes *et al.*, 2001). Saha *et al.* (2002) explained that at low added metal concentrations metals are mainly adsorbed onto specific adsorption sites, while at higher metal inputs soils lose some of their ability to bind heavy metals as adsorption overlabs, becoming thus less specific for a particular metal. This in turn induces a reduction in metal sorption.

The calculated constants for the linear Langmuir model are presented in Tables 3 & 4. The trends of Cu, Zn and Mn sorption indicated by the slope of the curves, in soil with compost this sorption intensity was higher than soil without compost. The explanation of this behaviour could be due to the high content and stability of the OM in soil with compost. The Cu could interact, forming stable complexes with high or low molecular weight organic substances (Naidu *et al.*, 1997 and Calace *et al.*, 2001). The Cu sorption behaviour in a competitive metal sorption system was not affected by the presence of Zn and Mn (Fig. 1 & 2); on the contrary, Zn and Mn sorption by soil was affected by the Cu, which reduced Zn and Mn sorption by soil components.

Chotpantarat *et al.* (2011) found that for multi-metal systems, the estimated retardation factors for the metals from highest to lowest were: $Pb^{2+} > Zn^{2+} > Ni^{2+} > Mn^{2+}$. For binary and multi-metal systems, the estimated sorption capacities of individual metals were found to be lower than the sorption capacities in single metal system - indicating possible competition for sorption sites.

The sorption amount Cu, Zn and Mn increased with amended compost. Organic matter is considered to play an important role in reducing plant uptake of heavy metals from soils due to its high CEC and complexing ability. Many authors have found that high organic matter content or addition of organic matter by organic amendments decreased the heavy metals concentration in solution (Walker *et al.*, 2003 and Karaca, 2004). This effect is attributed to the high CEC of organic matter and its ability to form chelate complexes with metals. Haghiri (1974) concluded that the decreased plant availability of heavy metal concentration with higher levels of organic matter added was predominantly due to the effect of increasing soil CEC.

The Q value for Cu was higher than other trace elements for S₄₀ and higher than the other soils with and without compost (Tables 3 & 4). The ratio of Q for trace elements was calculated. The average ratio of Q_{Cu}/Q_{Zn} and Q_{Cu}/Q_{Mn} was higher than the other ratios, indicating that the soils had higher affinity for Cu than other metals. The bonding energy coefficient varied with soil type and metal solution and all soils showed greater affinity for Cu than the other metals (Tables 3 & 4).

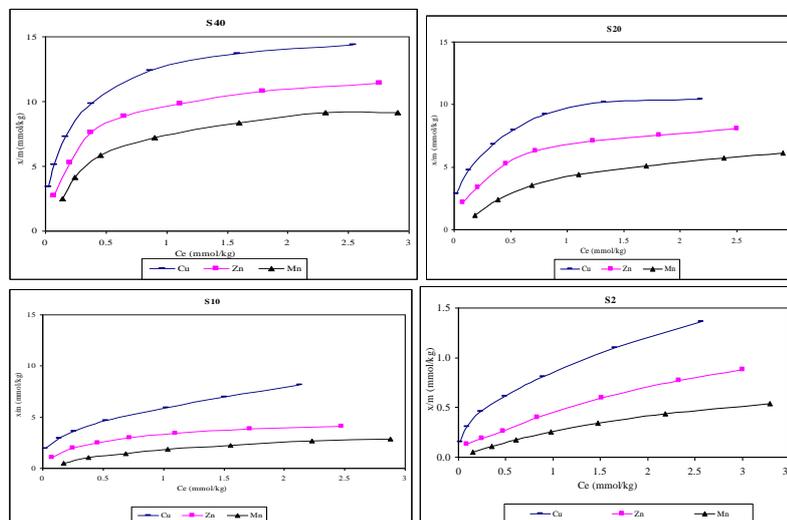


Fig.1. The adsorption of heavy metals by soils without compost as a function of the metal equilibrium concentration in solution.

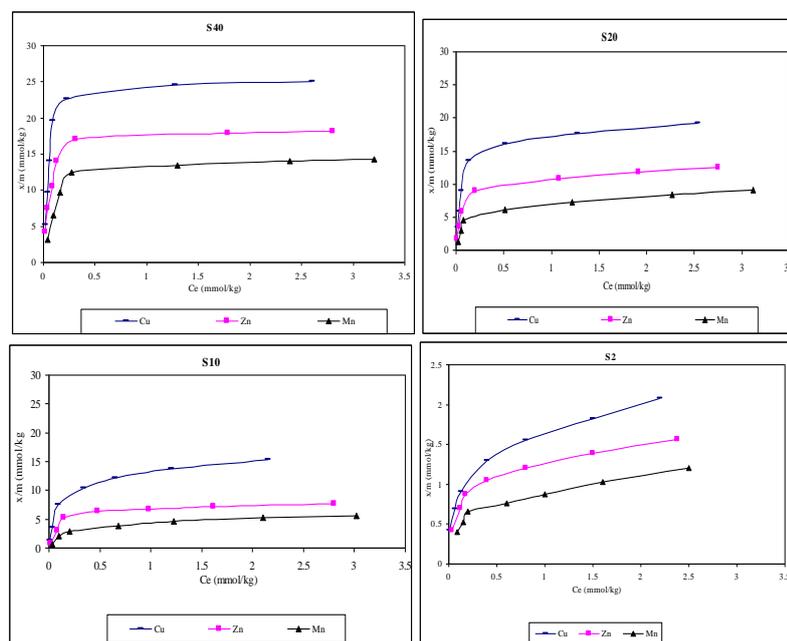


Fig.2. The adsorption of heavy metals by soils with compost as a function of the metal equilibrium concentration in solution.

Although, Harter (1984) and Sparks (1995) indicated that binding strength estimates made from sorption isotherms should only be considered qualitatively, they have been related to the free energy change of adsorption of different species (Van Riemsdijk *et al.*, 1986). Higher bonding energy coefficient values have been related to specifically sorbed metals at high energy surfaces with low dissociation constants (Serrano *et al.*, 2005). Lower bonding energy coefficient values appear to be related to sorption on low energy surfaces with high dissociation constants (Adhikari and Singh, 2003). Addition of compost increases more binding sites for the heavy metals at the surface of the soil, the compost lose their protons at increasing pH and become negatively charged and causing electrostatic binding towards heavy metals. Heidmann *et al.* (2005) found that addition of the fulvic acid to the clay strongly increased the metal sorption onto kaolinite at all studied pH.

The calculated constants for the linear Freundlich model are presented in Tables 5-6. The distribution coefficient represents the sorption affinity of the metal cations in solution for the soil solid phase and can be used to characterize the mobility and retention of trace elements in a soil system. A distribution coefficient can be related to both plant uptake and environmental pollution. Low distribution coefficients indicate that most of the metals present in the system remain in the solution and are available for transport, chemical processes, and plant uptake (Morera *et al.*, 2001); whereas higher values indicate lower mobility and higher retention of metals in the soil.

The K_d for soil without compost for each metal ranged from 0.87 to 12.10 l kg^{-1} for Cu, 0.46 to 9.12 l kg^{-1} for Zn and 0.24 to 6.9 l kg^{-1} for Mn (Tables 5 & 6). Mn showed the lowest K_d values regardless of the soil sample, while Cu K_d were generally the highest. When comparing soils, the lowest K_d values were obtained in the S_2 without compost, which correspond to the samples with the highest sand fractions and also the lowest CEC and Fe_2O_3 content among mineral soils. This relates to the fact that distribution of trace elements in soils is known to follow particle size distribution (Hartyáni *et al.*, 2000), with the lowest sorption capacity related to the sand fraction, due to the lower surface area associated with larger particle size fractions (Jain and Ram, 1997). The fact that S_2 without compost show the lowest organic carbon and CaCO_3 contents also provoked a reduced sorption capacity due to the low presence of other sorbing phases, such as organic matter and carbonates. On the contrary, the highest K_d values corresponded to S_{40} for all metals, the high K_d values were expected, due to the high clay fraction (Hartyáni *et al.*, 2000). Additionally, S_{40} had high pH and carbonate content, which enhances heavy metal retention (Adhikari & Singh, 2003 and Ponizovsky & Tsadillas, 2003).

On the other hand, the K_d for soil with compost for each metal ranged from 1.6 to 24.8 l kg^{-1} for Cu, 1.3 to 17.23 l kg^{-1} for Zn and 0.91 to 12.3 l kg^{-1} for Mn. When comparing soils, S_{40} with compost had the higher K_d values for all trace elements. Its high CEC and clay content were responsible for the highest sorption capacity among the soils considered. Additionally, organic matter content and neutral pH controlled metal sorption here. This fact may be related to the high affinity of organic matter for Cu at neutral pH (Alberti *et al.*, 1997). *Egypt. J. Soil Sci.* **55**, No. 1 (2015)

Hossain *et al.* (2009) noticed the dominance of organic bound fraction was observed for Cu, especially in organic rich surface soil. While S_2 with and without compost showed the lowest K_d for Cu, Zn and Mn, respectively. In general, copper was the trace element had the higher K_d values, showing that this is the most retained cation. The metals with the lowest K_d values were Zn and Mn, indicating that, when in competition, they are easily exchanged and substituted by Cu. The metal binding sites in compost is clearly more selective for Cu than Zn and Mn. It can, however, be argued that the effect of compost would have been greater than this if surface soils were used for this study because the compost present in the soil was likely to be physically and chemically stabilized and protected by mineral colloids (Gomez *et al.*, 2001).

According to the Q values and K_d , the selectivity sequence for the trace elements was $Cu > Zn > Mn$. This is in agreement with the findings of Hossain *et al.* (2009) who stated that Cu was not affected by competition while Zn and Ni were affected by competition of coexisting metals. In general, the relative selectivity of heavy metals is related to some relevant metal properties. The predicted affinity sequences of metals based on of their ionic radii, atomic weight, electronegativity, hydrolysis constant, and softness (Veeresh *et al.*, 2003 and Vega *et al.*, 2006).

In order to configure the relationship of clay content with the maximum adsorption (Q) for Cu, Zn and Mn, and the distribution (partition) coefficient (K_d), equations of various kinds were statistically fitted to the model parameters. Graphs of the fitted equations form are shown in Fig. 3 & 4. All the fitted equations are linear form in the amended soil, while in unamended the equations are polynomial, logarithm and power. This indicates that the clay minerals appear to be good indicators of predicting heavy metal adsorption. The presence of clay minerals as dominant may ensure a high metal sorption capacity that is an important factor regulating the sorption of heavy metals by soils (Serrano *et al.*, 2005).

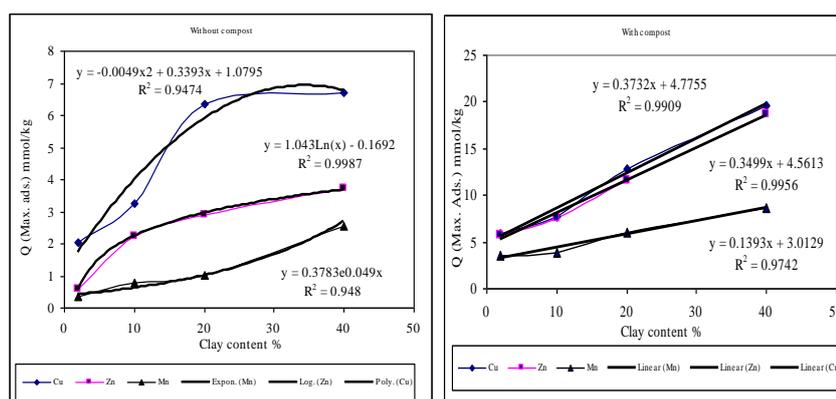


Fig. 3. The statistical relationship between clay content and maximum adsorption with and without compost.

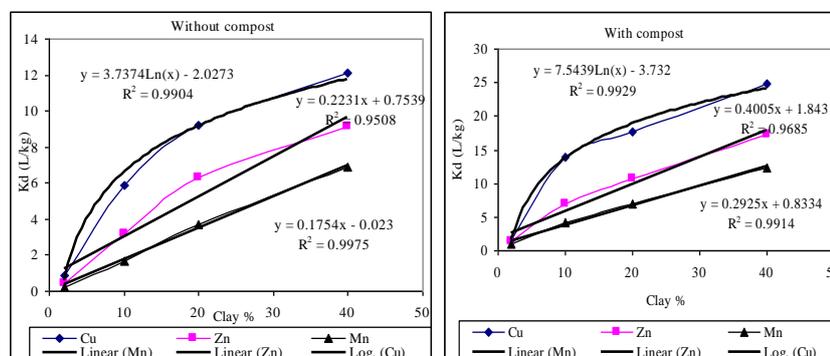


Fig. 4. The statistical relationship between clay content and K_d with and without compost.

Conclusion

A detailed investigation of competitive sorption processes between trace elements using sorption isotherms was performed in four soils with different clay contents (2%, 10%, 20% and 40%) with and without compost. The sorption capacity of the soils for Cu as measured by the estimated Q parameter from the Langmuir equation was greater than for Zn and Mn with and without compost. In general, selectivity sequences for trace elements in all soils, as determined by distribution coefficient using K_d and Q, led to similar conclusions. The prevalent adsorption sequences found were $\text{Cu} > \text{Zn} > \text{Mn}$. In general, Cu was sorbed in greater amount with binding strength compared to Zn and Mn. This suggests that sorption does not only depend on the element, but also on the soil reactive phase and on the element concentration. The generally greater distribution coefficient led to better retention of trace elements against leaching. The results showed that for competitive adsorption, the soil properties that were most strongly related to trace element adsorption were clay, CEC and OM content.

References

- Abdel-Rahman, G. (2009) Impact of compost on soil properties and crop productivity in the Sahel North Burkina Faso. *Amer-Eurasian J. Agr. Environ. Sci.* **6**, 220-226.
- Adhikari, T. and Singh, M.V. (2003) Sorption characteristics of lead and cadmium in some soils of India. *Geoderma*, **114**, 81-92.
- Alberti, G, Cristini, A., Loi, A., Melis, P. and Pilo, G. (1997) Copper and lead sorption by different fractions of two Sardinia soils. In: Prost R. (Ed.). *Contaminated Soils*. Les Colloques Paris: INRA Editions; CD: 036.PDF.
- Alloway, B.J. (1995) Soil processes and the behaviour of metals. In: Alloway, B.J. (Ed.), *Heavy Metals in Soils*. Blackie Academic & Professional, London, pp. 11–37.

- Appel, C. and Ma, L. (2002)** Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils. *Journal of Environmental Quality*, **31**, 581–592.
- Ashworth, J., Keyes, D., Kirk, R. and Lessard, R. (2001)** Standard procedure in the hydrometer method for particle size analysis. *Comm. Soil Sci. Plant Anal.* **32**, 633–642.
- Benito, M., Masaguer, A., Moliner, A., Arrigo, N. and Palma, R.M. (2003)** Chemical and microbiological parameters for the characterisation of the stability and maturity of pruning waste compost. *Biol. Fertil. Soils*, **37**, 184–189.
- Barber, S.A. (1995)** *Soil Nutrient Bioavailability. A Mechanistic Approach*. John Wiley & Sons, New York. ed. 2.
- Basta, N.T. and Tabatabai, M.A. (1992)** Effect of cropping systems on adsorption of metals by soils: III. Competitive adsorption. *Soil Sci.* **153**, 331–337.
- Calace, N., Liberatori, A., Petronio, B.M. and Pietroletti, M. (2001)** Characteristics of different molecular weight fractions of organic matter in landfill leachate and their role in soil sorption of heavy metals. *Environmental Pollution*, **113**, 331–339.
- Chaturvedi, R.K. and Sanker, K. (2004)** Soil analysis. In: “*Laboratory Manual for the Physico-Chemical Analysis of Soil, Water and Plant*”, Wildlife Institute of India, pp. 6–24.
- Chorom, M., Karkaragh, R.M., Kaviani, B. and Kalkhajeh, Y.K. (2013)** Monometal and competitive adsorption of Cd, Ni, and Zn in soil treated with different Contents of cow manure. *Applied and Environmental Soil Science*, Article ID 510278, 8 pages.
<http://dx.doi.org/10.1155/2013/510278>.
- Chotpantarat, S., Ong, S.K., Sutthirat, C. and Osathaphan, K. (2011)** Competitive sorption and transport of Pb²⁺, Ni²⁺, Mn²⁺, and Zn²⁺ in lateritic soil columns. *J. Hazard Mater.* **190** (1–3), 391–6.
doi: 10.1016/j.jhazmat.2011.03.058. Epub 2011 Mar 23.
- Evans, L.J. (1989)** Chemistry of metal retention by soils—several processes are explained. *Environ. Sci. Technol.* **23**, 1046–1056.
- Ghasemi-Fasaee, R. and Bahraminia, M. (2013)** Synergistic relationships in sorption characteristics of zinc and copper onto natural zeolite. *International Journal of Agronomy and Plant Production*. **4** (11), 3045–3049.
<http://www.ijappjournal.com/wp-content/uploads/2013/07/3045-3049.pdf>
- Gomes, P.C., Fontes, M.P., da Silva, A.G., Mendoca, E.S. and Netto, A.R. (2001)** Selectivity sequence and competitive adsorption of heavy metal by Brazilian soils. *Soil Sci. Soc. Am. J.* **65**, 1115–1121.
- Haghiri, F. (1974)** Plant uptake of cadmium as influenced by cation exchange capacity, organic matter, zinc, and soil temperature. *Journal of Environmental Quality*, **3**(2), 180–183.

- Harter, R.D. (1984)** Curve-fit errors in Langmuir adsorption maxima. *Soil Sci. Soc. Am. J.* **48**, 749-752.
- Harter, R.D. (1992)** Competitive sorption of cobalt, copper, and nickel ions by a calcium- saturated soil. *Soil Science Society of America Journal*, **56** (2), 444-449.
- Hartyáni, Z., Dávid, E, Szabó, S., Szilágyi, V., Horváth, T. and Tóth, A.H. (2000)** Determination of the trace elements distribution of polluted soils in Hungary by X-ray methods. *Microchem. J.* **67**, 195–200.
- Heidmann, I., Christl, I. and Kretzschmar, R. (2005)** Sorption of Cu and Pb to kaolinite–fulvic acid colloids, Assessment of sorbent interactions. *Geochim. Cosmochim. Acta*, **69**, 1675-1686.
- Hooda, P.S. and Alloway, B.J. (1994)** Sorption of Cd and Pb by selected temperate and semi-arid soils: effects of sludge application and ageing of sludge soils. *Water Air Soil Pollut.* **74**, 235-250.
- Hossain, M.A., Furumai, H. and Nakajima, F. (2009)** Competitive adsorption of heavy metals in soil underlying an infiltration facility installed in an urban area. QIWA Publishing 2009, *Water Science & Technology-WST* | 59.2 | 2009. <http://teacher.buet.ac.bd/abed/publication/059020303.pdf>
- Illera, V., Walter, I., Souza, P. and Cala, V. (2000)** Short-term effects of biosolid and municipal solid waste applications on heavy metals distribution in a degraded soil under a semi-arid environment. *The Science of the Total Environment*, **255**, 29-44.
- Jain, C.K. and Ram, D. (1997)** Adsorption of lead and zinc on bed sediments of the river Kali. *Water Res*; **31**(1), 154-62.
- Jalali, M. and Moradi, F. (2013)** Competitive sorption of Cd, Cu, Mn, Ni, Pb and Zn in polluted and unpolluted calcareous soils. *Environ Monit Assess.* **185** (11), 8831-46.
- Karaca, A. (2004)** Effect of organic wastes on the extractability of cadmium, copper, nickel, and zinc in soil. *Geoderma*, vol. **122**, no. 2-4, pp. 297-303.
- Larney, F.J., Olson, A.F., Miller, J.J., DeMaere, P.R., Zvomuya, F. and McAllister, T.A. (2008)** Physical and chemical changes during composting of wood chip-bedded and straw-bedded beef cattle feedlot manure. *J. Environ Qual.* **37**, 725-735.
- Martin-Garin, A., Gaudet, J.P., Charlet, L. and Vitart, X. (2002)** A dynamic study of the sorption and the transport processes of cadmium in calcareous sandy soils. *Waste Manage.* **22**, 201–207.
- Melero, S., Madejon, E., Ruiz, J.C. and Herencia, J.F. (2007)** Chemical and biochemical properties of a clay soil under dryland agriculture system as affected by organic fertilization. *European J. Agron.*, **26**, 327-334.
- Morera, M.T., Echeverria, J.C., Mazkarian, C. and Garrido, J.J. (2001)** Isotherm and sequential extraction procedures for evaluating sorption and distribution of heavy metals in soils. *Environ. Pollut.* **113**, 135–144.

- Mulvaney, R.L., Khan, S.A., Hoef, R.G. and Brown, H.M. (2001)** A soil organic nitrogen fraction that reduces the need for nitrogen fertilization. *Soil Soc. Am. J.*, **65**, 1164-1172.
- Naidu, R., Kookana, R.S., Summer, M.E., Harter, R.D., Tiller, K.G., (1997)** Cadmium sorption and transport in variable charge soils: a review. *Journal of Environmental Quality*, **26**, 602-617.
- Nelson, D.W. and Sommers, L.E. (1982)** Soil texture influence on applied nitrogen recovery. *Agron. J.*, **59**, 272-275.
- Ostroskia, I.C., Barros, M.A.S.D., Silvab, E.A., Dantasa, J.H., Arroyoa, P.A. and Lima, O.C.M. (2009)** A comparative study for the ion exchange of Fe (III) and Zn(II) on zeolite NaY. *Journal of Hazardous Materials*, **161**, 1404-1412.
- Ponizovsky, A.A. and Tsadillas. C.D. (2003)** Lead (II) retention by Alfisol and clinoptilolite: cation balance and pH effect. *Geoderma*, **115**, 303-12.
- Rashad, F.M., Kesba, H.H., Saleh, W.D. and Moselhy, M.A. (2011)** Impact of rice straw composts on microbial population, plant growth, nutrient uptake and root-knot nematode under greenhouse conditions. *Afr. J. Agric. Res.* **6**, 1188-1203.
- Rhoades, J.D. (1982)** Cation exchange capacity. In: “*Methods of Soil Analysis*, Part 2, *Chemical and Microbiological Properties*, Second Edition” (Ed. Page, A.L.; Miller, R.H. and Keeney, D.R), American Society of Agronomy, Inc, SSSA, Inc., pp. 149-157.
- Ryan, J., Estefan, G. and Abdul Rashid (2001a)** Soil nutrients sodium and anion analysis. In: “*Soil and Plant Analysis Laboratory Manual*, 2nd edition”, International Center for Agricultural Research in the Dry Area (ICARDA) and the National Agricultural Research Center (NARC), pp. 55-122.
- Ryan, J., Estefan, G. and Abdul Rashid (2001b)** Soil chemical analysis. In: “*Soil and Plant Analysis Laboratory Manual*, 2nd edition”, International Center for Agricultural Research in the Dry Area (ICARDA) and the National Agriculture Research Center (NARC), pp. 37-54.
- Saha, U.K., Taniguchi, S. and Sakurai, K., (2002)** Simultaneous adsorption of cadmium, zinc, and lead on hydroxyaluminum- and hydroxyaluminosilicate complexes. *Soil Sci. Soc. Am. J.* **66**, 117-128.
- Serrano, S., Garrido, F., Campbell, C.G. and Garcia-Gonzalez, M.T. (2005)** Competitive sorption of cadmium and lead in acid soils of Central Spain. *Geoderma*, **124**, 91-104.
- Sparks, D.L. (2003)** Sorption phenomena on soils. In: “*Environmental Soil Chemistry* 2nd ed.” Academic Press. Elsevier Science (USA), pp. 133-186.
- Sparks, D.L. (1995)** *Environmental Soil Chemistry*. Academic Press, San Diego, CA, p. 267.

- Ucer, A., Uyanik, A. and Aygun, S.F. (2006)** Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by tannic acid immobilised activated carbon. *Separation and Purification Technology*, **47**, 113-118.
- Van Riemsdijk, W.H., Bolt, G.H., Koopal, L.K. and Blaakmeer, J. (1986)** Electrolyte adsorption on heterogeneous surfaces: adsorption models. *J. Colloid Interface Sci.*, **109** (1), 219-228.
- Veeresh, H., Tripathy, S., Chaudhuri, D., Hart, B.R. and Powell, M.A. (2003)** Competitive adsorption behavior of selected heavy metals in three soil types of India amended with fly ash and sewage sludge. *Environ. Geol.* **44**, 363-370.
- Vega, F.A., Covelo, E.F. and Andrade, M.L., (2006)** Competitive sorption and desorption of heavy metals in mine soils: Influence of mine soil characteristics. *J. Colloid Interface Sci.* **298**, 582-592.
- Voegelin, A. and Kretzschmar, R., (2003)** Modelling sorption and mobility of cadmium and zinc in soils with scaled exchange coefficients. *Eur. J. Soil Sci.* **54**, 387-400.
- Walkley, A. and Black, I.A. (1934)** An examination of the wet method for determining organic carbon in soils: effect of variations in digestion conditions and of inorganic soil constituents. *Soil Sci. Plant Nutr.* **63**, 251-263.
- Walker, D. J., Clemente, R., Roig, A. and Bernal, M. P. (2003)** The effects of soil amendments on heavy metal bioavailability in two contaminated Mediterranean soils, *Environmental Pollution*, **122** (2), 303-312.
- Walter, I., Mart'inez, F., Alonso, L., Gracia, J. and Cuevas, G. (2002)** Extractable soil heavy metals following the cessation of biosolids application to agricultural soil. *Environmental Pollution*, **117**, 315-321.
- Zhou, L.X. and Wong, J.W.C. (2001)** Effect of dissolved organic matter from sludge and sludge compost on soil copper sorption. *Journal of Environmental Quality*, **30**, 878-883.
- Zhu, B. and Alva, A.K. (1993)** Differential adsorption of trace metals by soils as influenced by exchangeable cations and ionic strength. *Soil Science*, **55** (1), 61-66.

(Received 18 / 5 / 2014;
accepted 10 / 6 / 2014)

الإدمصاص التنافسي لعناصر النحاس والزنك والمنجنيز على أراضى مختلفة المحتوى الطيني ومعاملة بالكمبوست

محمد صلاح قطب

قسم الأراضى والمياه- كلية الزراعة - جامعة القاهرة - مصر .

تهدف هذه الدراسة الى تقييم أثر اضافة 5 ٪ كمبوست نباتي الى أربعة أنواع من الأراضى الرسوبية مختلفة القوام بنسب طين 2، 10، 20، 40 ٪ ثم التحضين لمدة 60 يوما لدراسة التنافس على مواقع الإدمصاص لمخلوط ثلاثة عناصر فلزية هي النحاس والزنك والمنجنيز لكلا من الأراضى الأصلية والمحضنة مع الكمبوست، تم تطبيق نموذج معادلة لانجمير وفرونديش واستخرج منها قيم الإدمصاص القصوى (Q_m) ومعامل التوزيع (K_d) . حيث أظهرت النتائج ارتفاع قيمة السعة الإدمصاصية لجميع العناصر على أسطح التربة المضاف اليها الكمبوست مقارنة بالأراضى الأصلية و كانت السيادة لعنصر النحاس مقارنة بالعناصر الأخرى وذلك لشدة ارتباطه بالمادة العضوية. كما أظهرت النتائج ترتيب قدرة العناصر الثلاثة في التنافس على مواقع الإدمصاص على أسطح التربة بناء على القيمة القصوى للإدمصاص ومعامل التوزيع لهذه العناصر على النحو التالي $Cu > Zn > Mn$. كما تبين أن نسبة الطين كان لها أثر كبير في زيادة قيم (Q_m) ، (K_d) .