

Immobilization of Heavy Metals in Contaminated Sites Using Natural Organic Materials

Mohamed L. Moharem¹, Tarek M. Omar², and Hesham M. Gaber³

¹ Regional center for Food and Feed, Agricultural Research center, Alexandria, Egypt

² Regional center for Food and Feed, Agricultural Research center, Cairo, Egypt

³ Faculty of Agriculture, Alexandria University, Alexandria, Egypt

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ABSTRACT

The current study was conducted to evaluate the utilization of some treated-organics such as clover and sludge to immobilize heavy metals (HMs) in contaminated sites. Due to the heterogeneous of the organic materials which contain solid and dissolved components, dissolved organic carbon (DOC) was removed from the clover and sludge organics-hereafter it called treated organics- to eliminate the potential impacts of DOC on heavy metals mobility through soil system. Sorption experiments were run in batch system to demonstrate the sorption behavior of Cd and Cu as a result of adding these treated/non-treated organics in three different soils types. the results showed that the addition of the non-treated clover and sludge organics to the soils significantly increased the mobility of metals in most cases, as expressed by Freundlich k_d values, which can attributed to DOC derived from the organics, and was more pronounced for Cu than for Cd. In contrast, when the soils were treated with the treated organics, the capacity of these soils to retain Cd and Cu increased depending on metal, soil, and organic type. Cd and Cu presented different degrees for binding sites of organics depending on components-molecular mass of these organics. Moreover, total and dissolved heavy metals content in the clover and sludge was measured. However, mobilization of Cu and Cd determined through desorption experiments indicated insignificant release of these heavy metals to the soil system. The final results revealed that those treated organics can be utilized as cheap immobilizing agents for heavy metals such as Cd and Cu in contaminated sites.

Key word: Heavy Metals, Immobilization, sorption, organic Immobilization

INTRODUCTION

Soils can receive heavy metals from various sources, mainly by application of fertilizers, pesticides, compost, animal manure, and sewage sludge (Adriano, 1986; Alloway, 1995). When concentration of these toxic metals elevated in soil ecosystem, it may pose a serious threat to the human health, through entering food chain, and natural ecosystem; consequently, remediation processes must be achieve to restore heavy metals-soil concentrations to the standard levels.

Conventional methods to remediate metal-contaminated soils (landfilling or excavation and extraction) can be used at highly contaminated sites but are not applicable to large areas. These remediation methods require high energy input and expensive machinery (Vangronsveld and Cunningham, 1998). In contrast, in situ immobilization of metals is a promising approach that has the potential to remove metals from solutions and/or stabilize metals in soils (Ma *et al.*, 1993). In other words, this approach involves minimization of contaminants mobility by transferring the metals from labile to nonlabile phases via physically, chemically, or biologically induced transformation; thus it can stabilize these toxic metals in a form less available for plant uptake

or leaching through soil profile. In this technique, a wide range of binding agents has been tested in laboratory and field conditions to reduce the solubility of heavy metal contaminants. For instance, chemical amendments including organic matter, alkaline materials, and phosphate fertilizer were used for chemical remediation of Pb, Cd, and/or Zn in contaminated soil. (Hooda and Alloway, 1996; Mench *et al.*, 1994; McGowen *et al.*, 2001).

Organic amendments are considered other immobilizing agents for metals such as Pb, Cd, and Zn in contaminated soil including municipal biosolids (sewage sludge), composts, manures, and peat (Brown *et al.*, 1997). Although these amendments may precipitate metals in soils (McBride, 1994), their dissolved components (dissolved organic carbon -DOC-) may enhance its mobility (Jordan *et al.*, 1997; Geebelen *et al.*, 2002; Moharem, 2008) and contribute to its uptake by plant roots (Albasel and Cottenie, 1985; Jin *et al.*, 2005, Moharem, 2008). However, Considerable uncertainty exists about the long-term fate of polluting trace metals contained in sewage sludge. One possibility is the stabilization and even a reduction of the trace metal availability to plants by progressive trace metal immobilization into less soluble forms such as occlusion in Fe and Al oxides or precipitation as silicates, phosphates, or

carbonates (Dowdy *et al.*, 1994; Brown *et al.*, 1998). Another possibility might be an increase of trace metal bioavailability and leaching through sewage sludge organic matter mineralization ("time bomb effect") (Zhao *et al.*, 1997). Field studies covering several decades have produced unclear results (Chang *et al.*, 1997; Logan *et al.*, 1997) and led to contradictory conclusions (McBride, 1995; McGrath *et al.*, 2000).

Such those organic amendments, like sewage sludge, are commonly used in some agricultural practices, and are considered as an alternative method for organic waste disposal by landfill. Also, clover is added to soils as a final harvest. These organics when reach the soils, they will provide the soils with both solid and dissolved components (DOC). These various components would govern the fate and behavior of heavy metals in soils with mainly different manner.

In current study, we attempt to eliminate the hazardous impact of using the organic amendments on the behavior of heavy metals in soils (by reducing the DOC content from some organics such as sewage sludge and clover-hay by washing them with distilled water several times); since these dissolved components could be responsible for enhancement heavy metals mobility in soils as mentioned above. So, this study aimed to elucidate whether these treated organics could be effectively utilized as cheap immobilizing agents for heavy metals in contaminated soils in comparison with their original component.

MATERIALS AND METHODS

Soils

Three soil samples differed in texture and calcium carbonate content were used in this study. Sandy soil (Typic Quart zipasmments) was collected from Elbostan 80 Km south west Alexandria, calcareous soil (Typic Calciorthids) from El-Nahda 40 Km south west Alexandria, and clay soil (Typic Torrifluvents) was collected from Tanta. Soil samples were air-dried, passed through a 2-mm

sieve and stored in plastic bags for latter use. Selected chemical and physical properties of the three soil samples are shown in Table 1. Soil pH was measured in 1:2 soil:water ratio and electric conductivity (EC) was measured in soil paste extract. The bioavailable Cd, Cu, and Pb were extracted by DTPA (Lindsay and Norvell, 1978) and measured by inductively coupled plasma (ICP) (Perkin Elmer Optima 2000 DV). Soil organic matter content was estimated by the method of Walky and Black (Nelson & Sommers, 1982), total carbonate equivalent was determined by the calcimeter method (Nelson, 1982), and cation exchange capacity was measured by the method of Rhoades (1982). Particle size distribution analysis was determined by the hydrometer method (Hillel *et al.*, 1972).

Organic Materials

Two sources of organic materials which commonly used as organic amendments in agricultural soils were chosen for the current study. The first one was air-dried sewage sludge obtained from Alexandria waste water treatment plant (N9) and the second was clover hay collected from the research station of faculty of agriculture, university of Alexandria (Abis). Sewage sludge was ground, passed through 2-mm sieve whereas clover hay was air-dried then dried in an oven at 70°C for three days, ground and stored in plastic bags.

Dissolved organic carbon (DOC) from clover hay (Cl) and sludge (Sl) was removed/minimized from both organics by sowing an known weight of Cl or Sl in 2L distilled water. The suspension was shaken for 2 h and left over night. Then, DOC in the suspension was removed by filtration. This process was repeated several times until the suspension being clear. Finally, sufficient amount of solid sludge or clover-straw was obtained. These solids, were air-dried, ground, and passed through 2-mm sieve. Hereafter, the obtained solids can be referring to DOC-removed organics (treated) that are different from the original organics.

Table 1: Selected chemical and physical characteristics of the three studied soils.

Soil	pH ^a	EC ^b dS m ⁻¹	Texture	CaCO ₃ %	OM	DTPA-extractable metal		CEC cmol Kg ⁻¹
						Cd	Cu	
Clay	8.29	0.75	clay	3	1.9	N.D.	2.81	33
Calcareous	8.33	4.56	sandy clay loam	22.4	1.5	N.D.	0.95	15
Sandy	8.26	3.19	sandy	3.6	0.4	N.D.	0.19	6

^apH was measured in 1:2 soil to water suspension.

^bEC was measured in soil paste extract.

Selected chemical properties of the two organics are shown in Table (2). Total concentrations of Cd and Cu in addition to other heavy metals in aqua regia digested pure organics extract (Esakku, *et al.*, 2005; Shrivastava and Banerjee, 1998) were measured by ICP. Moreover, these heavy metals were also measured in the DOC of the two studied organics. Also, the release of these metals from the sludge to the soil system was tested during 24 h desorption experiment using 0.03 mM CaCl_2 . The organic matter content was estimated by the method of Walky and Black (Nelson & Sommers, 1982).

Sorption Experiments

Sorption experiments were conducted in order to examine the sorption behavior of Cd and Cu in the absence and presence of treated organics for the studied soils. Also the metals-sorption behavior with these treated organics was conducted in comparison with these original organics.

Cd(II) and Cu(II) sorption isotherms were obtained using the batch equilibration procedure. Initial metal concentrations were 5, 10, 20, 40, 80, and 160 mg L^{-1} . Volume of 20 ml $\text{Cd}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$ dissolving in a 3 mM CaCl_2 solution as background with metal ion concentrations range was added to 3.25 or 3.5 g soil in a 50-ml centrifuge tube (representing control samples for clover and sludge respectively, and this difference in soil weight is due to the difference in density of the clover and sludge organics). Samples were equilibrated for 12 h, as expected time for equilibration, by a horizontal shaker (200 rpm). The experiment was conducted at room temperature ($\approx 25^\circ \text{C}$) and included triplicate samples and appropriate blanks of each soil and metal. After equilibration, the suspensions were centrifuged, and 10mL of the supernatant solution was removed for analysis. The supernatant was acidified by 2 drops of HNO_3 (70%) and stored in a refrigerator for analysis. The concentration of heavy metal in the supernatant was determined by the ICP. The amount of metal sorbed was calculated as the difference between the initial and final solution concentrations.

To study the effect of clover and sludge organics (treated or non-treated) on the sorption behavior of the studied heavy metals, the above sorption experiment was repeated with some modifications. Volumes of 20 ml of the metal solution were added to 3 g soil and 0.25 g clover or 2.5 g soil and 1 g sludge in the centrifuge tube. Shaking, centrifugation, and analysis were run as previously described.

RESULTS AND DISCUSSIONS

Cd and Cu Sorption Isotherm

Figures 1 and 2 give the sorption isotherms of Cd and Cu of the studied soils without addition of organic materials. Sorption isotherm data showed that the calcareous and clay soils had the highest affinity for Cd whereas the sandy soil exhibited the least affinity. This result could be related to the variation in soil properties. It is noted from Table (1) that sandy soil has the lowest values of organic matter, clay content, calcium carbonate content, and cation exchange capacity. These soil properties may explain the lower affinity of the used sandy soil to retain Cd. In contrary, the high values of properties mentioned above may be responsible for the high amount of Cd retained by the clay soil whereas with calcareous soil the high content of calcium carbonate may be the reason for such increase in Cd retention by this soil. Many researchers demonstrated the role of soil-calcium carbonate in Cd retention which is interpreted to Cd precipitation with CaCO_3 (Bataillard *et al.*, 2003; and Temminghoff *et al.*, 1995). The sorption isotherms of calcareous and clayey soils were characterized by H-curve isotherm indicating a strong affinity for these soils for Cd while for sandy soil was characterized by a decreasing slope as equilibrium concentration increased which referred to as L-type (Fig.1). This classification is referred to as the isotherm classification proposed by Giles *et al.* (1960) who distinguished four main types of isotherms corresponding to different solute adsorbent interactions. This classification has been used lately to describe heavy metals sorption on soils (Harter, 1983).

Table 2: Organic matter content and heavy metals concentration in pure organic materials and their DOC. extractants.

Organics	O.M (%)	H.M Concentration (mg L^{-1})													
		Cd		Cu		Pb		As		Co		Ni		Fe	
		org.	DOC	org.	DOC	org.	DOC	org.	DOC	org.	DOC	org.	DOC	org.	DOC
Clover hay	34.29	0.648	0.002	9.656	0.047	0.127	N.D.	N.D.	N.D.	0.705	0.001	3.374	0.006	343.1	0.260
Sewage sludge	49.12	0.446	0.003	388.8	0.069	222.3	0.019	3.456	0.001	20.36	0.002	31.46	0.017	108.7	0.434

N.D., not detected; org., organic materials

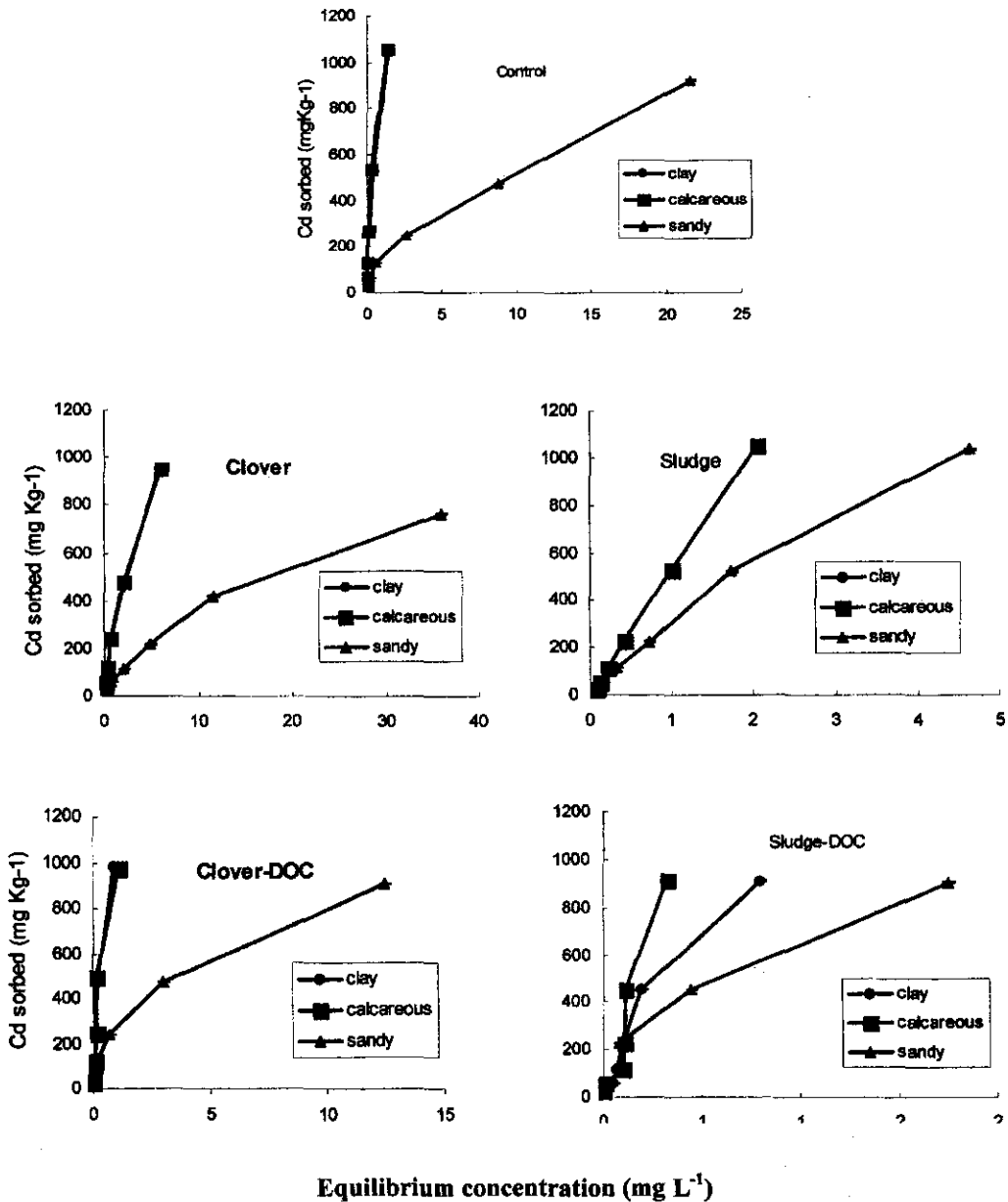


Fig. 1: Cadmium sorption isotherm onto the three studied soils as affected by different treatments.

The clayey soil exhibited the highest affinity for Cu sorption while the sandy soil exhibited the least affinity. Copper is known to form strong complexes with organic matter and speciation studies that extracted the organic fraction from biosolids-amended soils before the oxide fraction, found most Cu existed in the organic fraction (McGrath and Cegarra, 1992). Also Paulo *et al.* (2001) pointed out that Cu adsorption by Brazilian soils was related to the amount of organic C, clay, and gibbsite. Thus,

the high values of clay and organic matter in studied clayey soils may be responsible for the high retained Cu. In contrary, the low values of mentioned properties for studied sandy soil could interpret the low Cu sorption. The sorption isotherms for clayey and calcareous soils were characterized by H-curve which indicates the high ability of clayey and calcareous soils to sorb Cu while sandy soil was characterized by L-curve (Fig 2).

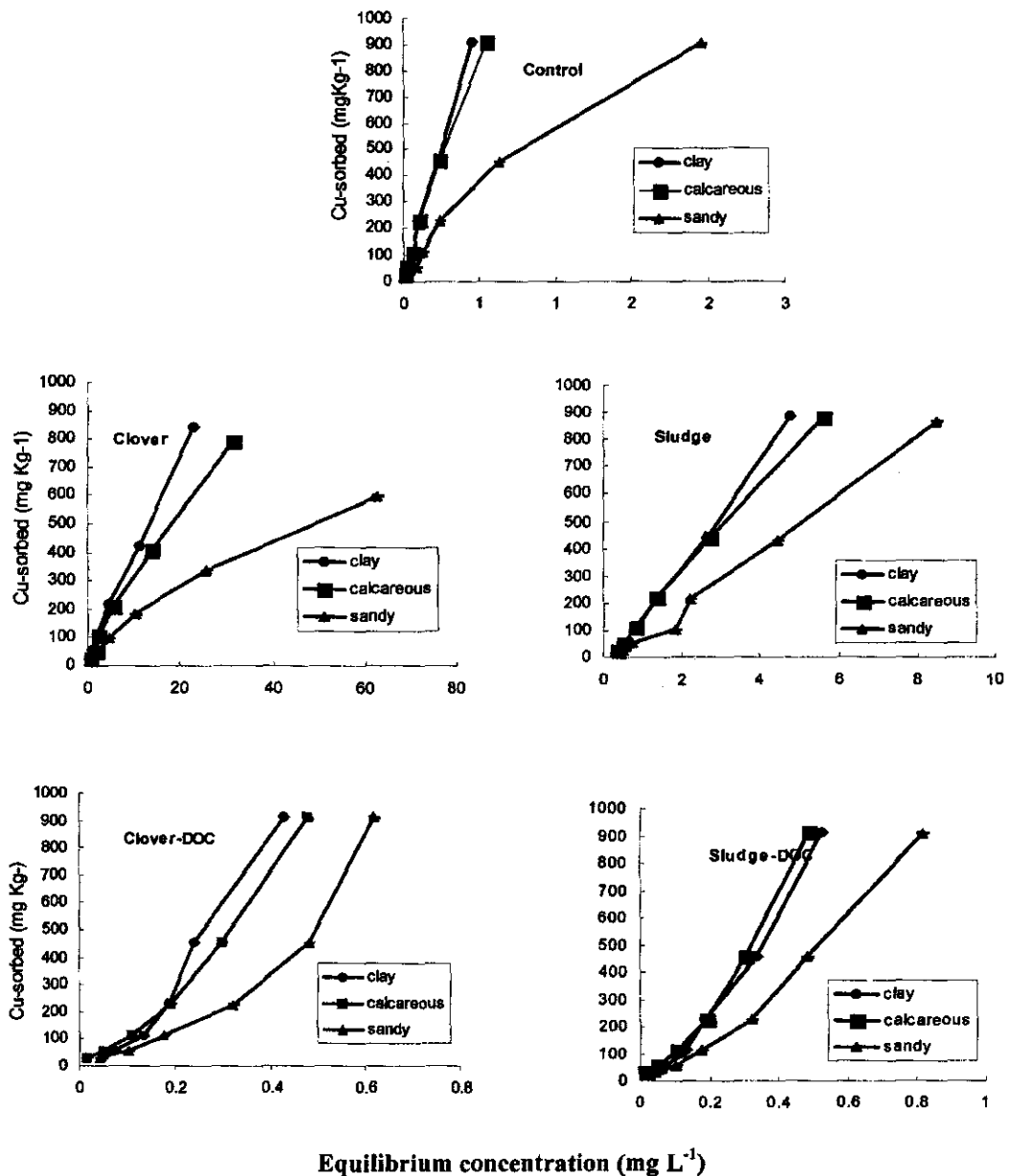


Fig. 2: Copper sorption isotherm onto the three studied soils as affected by different treatments.

Sorption Equilibrium Model

The Cd and Cu sorption data were plotted according to the Freundlich model. The general form of Freundlich model is:

$$S = K_d C^n$$

Where S is the amount of metal sorbed by the solid phase (mg/Kg), C is the equilibrium metal concentration in liquid phase (mg/L), K_d is the distribution coefficient (mL/g), n is the empirical constant describing sorption (non) linearity. The Cd and Cu sorption isotherms confirmed better to the Freundlich equation than to the Langmuir equation (data not shown) as indicated by the high values for

the correlation coefficient of determination (R^2). This may be explained by the assumptions inherited in the Langmuir model which may not be valid for a heterogeneous soil system. Freundlich model successfully described the two metals sorption over an initial concentration range between 5 and 160 mg/L. Freundlich isotherms for the two metals and three soils studied are shown in Fig. (3). Also Freundlich parameters and their R^2 values are shown in Tables 3 and 4.

Distribution coefficients (K_d) indicate the capability of a soil to retain a solute and also the extent of its mobility in a liquid phase (Reddy and Dunn, 1986). According to Alloway (1995), 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.

For Cd, average Freundlich K_d values were ranged from 175.1 (sandy soil) to 962.35 and 959.74 for calcareous and clay soils respectively (Table 3). These results coincide with and validate the data depicted previously in Fig (1).

For Cu, average K_d values were ranged from 576.78 (sandy soil), which represent the lowest value, to 2196.14 (clayey soil), representing the highest value (Table 4). These results again coincide with and validate the data described in Fig (2).

Effect of Organics on Metals Sorption

Effect of non-treated organics

Figures 1 and 2 illustrate sorption isotherms of Cd and Cu respectively as affected by clover or sludge organics. Also Tables 3 and 4 show sorption parameters calculated from Freundlich model and their R^2 for Cd and Cu, respectively.

However, none observed change in isotherm-shapes as a result of organics addition for the two studied metals except for Cu-sorption isotherm in sandy soil which changed from L-type to S-type as affected by sludge amendment indicating the strong effect of this sludge on decreasing Cu sorption.

For Cd, the addition of the clover hay and sewage sludge significantly decreased the K_d values for the studied soils except for sandy soil for the sludge treatment. For clay and calcareous soils, the clover treatment was more effective in decreasing K_d value than the sludge treatment since it decreased the K_d value from 956.75 to 256.04 and 958.74 to 255.45 whereas with the sludge, such decrease was from 962.72 to 530.4 and from 965.96 to 491.25 for these two soils respectively. Addition of the clover to sandy soil decreased the K_d value from 174.42 to 65.74, whereas the addition of the sludge increased the K_d value from 175.78 to 289.93 (Table 3 and Fig 4).

In case of Cu, soil amendment with the clover and sludge significantly decreased the K_d values of the three studied soils. For instance, the addition of the clover decreased the K_d value from 2363.2 to 55.71, from 1389.00 to 42.54, and from 629.36 to 27.39 for clay, calcareous, and sandy soils respectively (Table 4 and Fig. 4).

Generally decrease of Cd and Cu sorption as expressed by K_d can be referred to the presence of dissolved organic carbon derived from the sludge and clover organics since many studies demonstrated that dissolved organic matter can facilitate metal mobility in soil towards groundwater by acting as a carrier through formation of soluble metal-organic complexes (Temminghoff *et al.*, 1997, Zhao *et al.*, 2007, Moharem, 2008). Moreover, Liu *et al.*, (2007) evaluated the influences

of sewage sludge-derived organic matters on heavy metals sorption through batch experiment. They demonstrated that dissolved organic matter in sludge significantly depressed the sorption ($p < 0.01$). Moreover, the contribution of DOC to metal transport is expected to be magnified as pH increases, although overall mobility is greater at low pH. This is due to the increased solubility (or mobility) of DOC and the very low solubility of metal ions in neutral to alkaline pH soils (Richards *et al.*, 2000). Hence, in the three alkaline soils studied in the current research the solubility of DOC is expected to be high.

Addition of organic treatments decreased the K_d values for the two studied metals except for Cd in sandy soil for the sludge treatment as mentioned above. The increase of k_d value in this case may be referred to the more preferably associate of Cd to the sludge-solid components existing on soil-sorptive surfaces than the dissolved components existing into aqueous phase since Cd demonstrated a tendency to preferably associate with larger, humified, and less soluble organic materials (Kaschl *et al.*, 2002). However, this was only for sandy soil which showed the lowest values for organic matter, clay content, calcium carbonate content, and cation exchange capacity; Hence, any new organic sorptive surfaces existence will be effective in Cd sorption than in the case of the other two studied soils which are characterized by high sorptive capacity. Moreover, this exception behavior of Cd in sandy soil may be interpreted according to Hoffmann *et al.* (1998) which studied an array of sandy soils, and observed that soil heavy metal content was highly correlated to soil organic matter content, thus suggesting that metals can be readily bond to soil particulated organic matter. This finding was only for the sludge but not for the clover hay in the same sandy soil which may be attributed to the different structure and molecular weight of the two organics.

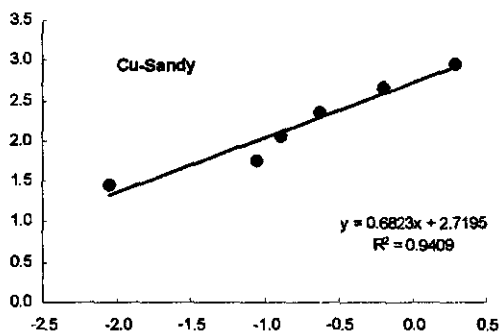
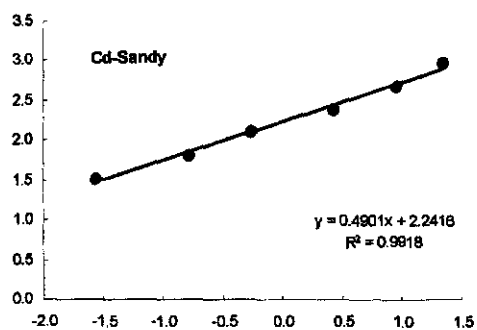
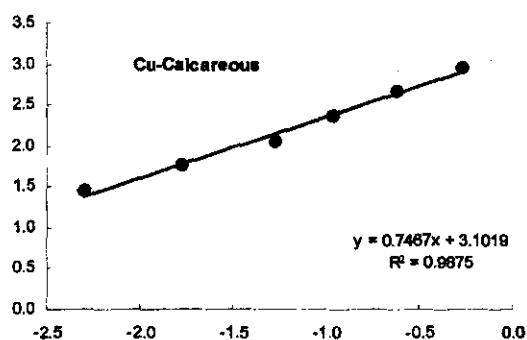
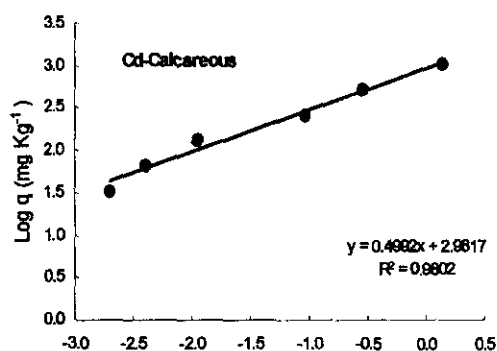
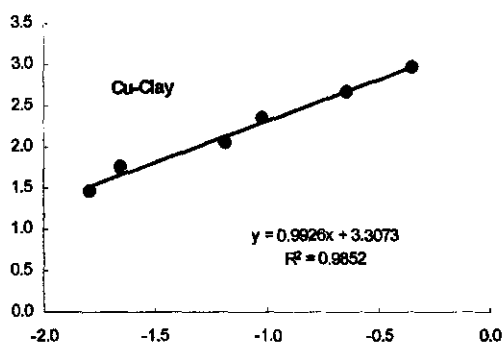
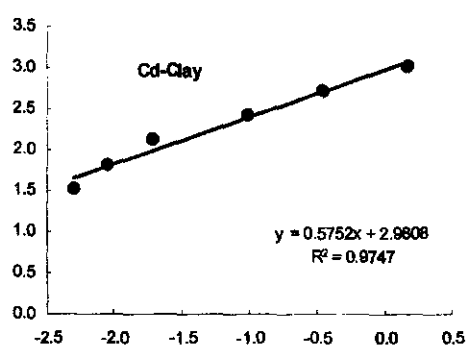
Effect of treated organic

Figures 1 and 2 illustrate sorption isotherms of Cd and Cu, respectively, as influenced by adding treated clover or sludge organics. Also Tables 3 and 4 show sorption parameters calculated from Freundlich model and their R^2 for Cd and Cu, respectively.

For Cd, the addition of both treated clover and sludge significantly increased the K_d values for the three soils. For instance, the addition of treated clover increased the K_d value from 956.75 to 1469.26, from 958.74 to 1019.06, and from 174.42 to 265.00 for clay, calcareous, and sandy soils, respectively; whereas the increase of K_d values as a results of adding treated sludge was from 962.72 to 1540.64, from 965.96 to 1170.85, and from 175.78 to 629.65 for clay, calcareous, and sandy soils, respectively (Table 3 and Fig. 4).

Table 3: Fitted Freundlich parameters of Cd derived from sorption isotherms for the three studied soils as affected by organic treatments.

Treatments	Clay			Calcareous			Sandy		
	K_d	n	R^2	K_d	n	R^2	K_d	n	R^2
Clover hay									
Control	956.75	0.76	0.89	958.74	0.72	0.91	174.42	0.46	0.96
Organic material	256.04	0.83	0.98	255.45	0.83	0.97	65.74	0.72	0.99
Without DOC	1469.26	0.78	0.87	1019.06	0.67	0.89	265.00	0.53	0.98
Sewage sludge									
Control	962.72	0.87	0.88	965.96	0.86	0.88	175.78	0.51	0.96
Organic material	530.4	0.95	0.97	491.25	0.92	0.99	289.93	0.86	0.99
Without DOC	1540.64	0.97	0.94	1170.85	0.56	0.89	629.65	0.51	0.94



Log C (mg L⁻¹)

Fig. 3: Freundlich sorption isotherm for Cd and Cu onto the three studied soils (control treatments).

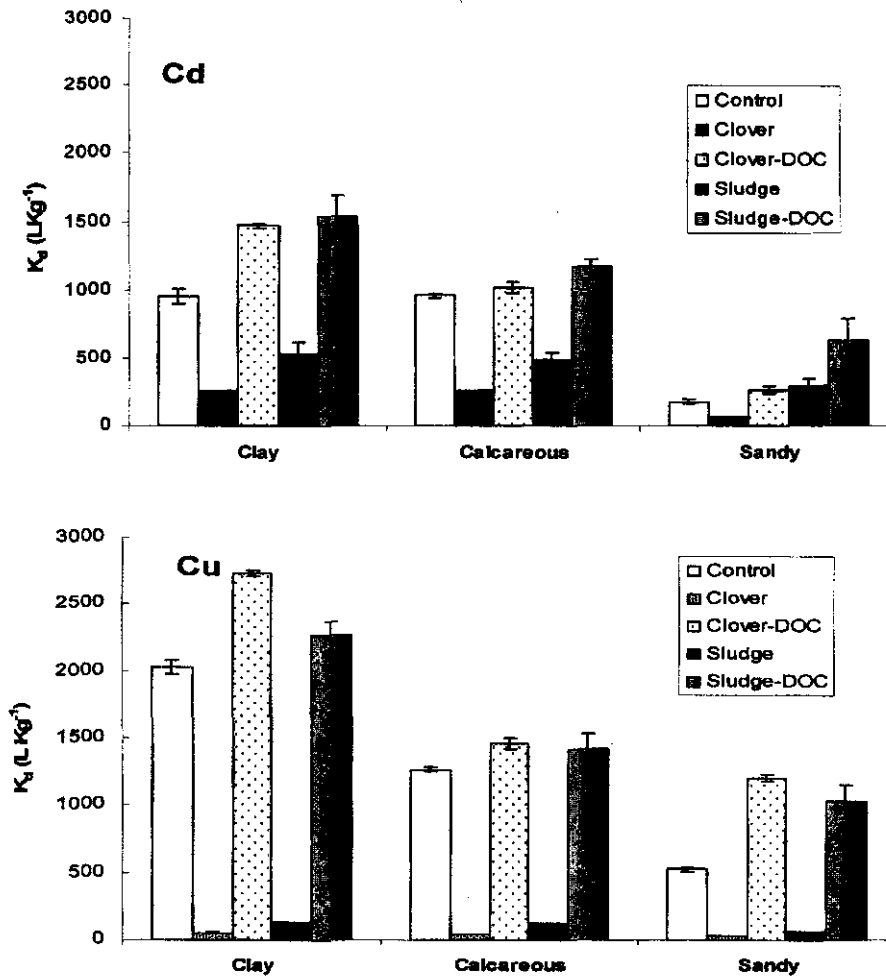


Fig. 4: Effect of treatments on K_d for Cd and Cu using the three studied soils.

For Cu, the addition of sludge increased the K_d values for the three studied soils. For instance, the addition of treated clover increased the K_d value from 2363.2 to 2732.50, from 1389.00 to 1456.8, and from 629.36 to 1204.48 for clay, calcareous, and sandy soils, respectively; whereas this increase of K_d value for treated sludge was from 2029.08 to 2263.08, from 1264.45 to 1422.00, and from 524.20 to 1023.06, respectively (Table 4 and Fig. 4).

However, after removal of dissolved components from clover and sludge (treated organics) which these components are responsible for increasing heavy metals mobility in studied soils, due to soluble organo-metal complexes as mentioned above, the rest components of these organics are less soluble components (solid phases), and thus can sorb the metals away from soil- aqueous phase. In case of the sludge, the solid composition of this biosolid depends on a large extent on the origin of the residues treated (i.e., wastewater from domestic or industrial activities). These solid components present, i.e., organic matter, oxyhydroxides of iron,

aluminium and manganese, phyllosilicate minerals, carbonates and sulfides. (Ure and Davidson, 2001). In addition, metal ions are retained on these solid components by different mechanisms (ion exchange, outer - and inner-sphere surface complexation (adsorption), precipitation or co-precipitation). For Agricultural solid waste materials, such as clover, are usually composed of lignin and cellulose as the main constituents (Demirbas, 2000a, b). The functional groups present in biomass molecules acetamido groups, carbonyl, phenolic, structural polysaccharides, amido, amino, sulphhydryl carboxyl groups alcohols and esters (Gupta and Ali, 2000) These groups have the affinity for metal and can bound by rather complex process affected by several mechanisms involving chemisorption, complexation adsorption on surface and pores, ion exchange, chelation, adsorption by physical forces, entrapment in inter and intrafibrillar capillaries and spaces of the structural polysaccharides network as a result of the concentration gradient and diffusion through cell wall and membrane (Qaiser *et al.*, 2007)

Table 4: Fitted Freundlich parameters of Cu derived from sorption isotherms for the three studied soils as affected by organic treatments.

DOC source	Clay			Calcareous			Sandy		
	K_d	n	R^2	K_d	n	R^2	K_d	n	R^2
Clover hay									
Control	2363.2	1.2	0.97	1389.00	0.83	0.97	629.36	0.90	0.99
Organic material	55.71	0.87	0.997	42.54	0.85	0.97	27.39	0.77	0.99
Without DOC	2732.50	1.63	0.99	1456.8	1.02	0.96	1204.48	1.28	0.97
Sewage sludge									
Control	2029.08	0.99	0.99	1264.45	0.75	0.99	524.20	0.68	0.94
Organic material	133.38	1.25	0.99	123.94	1.23	0.98	64.85	1.23	0.98
Without DOC	2263.08	1.44	0.99	1422.00	1.02	0.96	1023.06	1.21	0.99

Metals Sorption and K_d Values

The effect of treated and non treated organics on increasing or decreasing metal sorption onto soils as expressed by K_d values varied between the two metals studied. To demonstrate such effect, the percentage of changing K_d value calculated with reference to the study control (without organics addition) of each treatment was obtained for each metal and soil (Table 5).

For non-treated organics, as mentioned previously, the addition of clover and sludge decreased the sorbed metal quantity in most cases for Cd and all cases for Cu which is related to DOC derived from these organics. Such effect was more pronounced for Cu than for Cd- as expressed by changing K_d value- which is known to complex with organics with high stability constant. For instance, the percentage of changing K_d value for clover and sludge for the three studied soils was more negativity (K_d decreased) for Cu than Cd (Table 5) - except for sludge treatment for Cd in sandy soil which is out of this comparison. Our results were in agreement with Klambert et al., 1989 which listed the stability sequence of the complexes for some selected cations with organic to be in the following order: $Fe^{3+} > Al^{3+} > Cu^{2+} > Pb^{2+} > Fe^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Mn^{2+}$. Thus, Cu with high stability constant than Cd is expected to be more affected with DOC than Cd.

For treated organics, DOC removal from clover and sludge changed the impact of addition of these organics on metal sorption resulting in increasing K_d values for the two studied metals as mentioned previously; since this effect was more pronounced for Cd than for Cu for the two organics except for clover treatment in sandy soil. This finding was demonstrated in Table 5 in which the percentage of changing K_d value for the sludge and the clover treating the three studied soils was more positively (K_d increased) for Cd than for Cu in most cases. This finding can be referred to the high affinity of Cd to complex with high molecular mass of organics (solid-organic matter) as mentioned above. This finding was reversed for the clover treatment in

sandy soil which Cu tends to appear high affinity for sorption than for Cd indicating by more positively (K_d increased) for Cu than Cd; however, the low mobility of Cu in clay and calcareous soils in control samples as indicated from high K_d values (Table 4) may obscure the impact of adding this treated organic via more sorption as appeared in sandy soil in which Cu characterized by relatively high mobility in this soil comparing with the other two soils. This result was only for the treated clover but not for the treated sludge which may be attributed to the different structure and molecular weight of the two organics leading to different degrees of metal binding to these components. Thus from this discussion, we can concluded that Cd and Cu can offer different degrees for binding sites of organics depending on components-molecular mass of these organics. Whereas Cd tends to associate with both solid component of treated organics (solid-organic mater) of clover and the dissolved organics (DOC) as expressed by relatively narrow range of changing K_d values (between + and -) comparing with Cu values, Cu can strongly bind with DOC derived from the both organics relatively rather than the solid phase which is expressed by wide range of changing K_d values toward negative changing K_d rather than positive K_d (Table 5). This finding can be confirmed by many researchers who demonstrated that Cu can hardly complex with DOC comparing with other metals (Japenga *et al.*, 1992; Del Castilho *et al.*, 1993).

Finally, from the discussion above we can conclude that the removal of DOC from both clover and sludge can convert the behavior of metals via more sorption for the soils treated with these organics. Thus, these treated organics can be utilized as cheap immobilizing agents for heavy metals such as Cd and Cu in contaminated sites; since these treated organics can increase the capacity of soil matrix to retain heavy metals in contaminated sites, thus it can stabilize the toxic metals in a form less available for plant uptake, so they can reduce heavy metals risks from entering food chain.

Environmental impacts of applying biosolid

The concentration of heavy metals in sludge is probably the main factor that limits the application of this material in agricultural soils; therefore it is important to examine the capability of natural soil conditions to release these metals from the resident sites existed into the sludge to the soil solution when this biosolid reaches soils. To evaluate such relation, total HMs content such as Cd, Cu, Pb, As, Co, Ni, and Fe was measured in both the digested sludge extract and in the DOC obtained from the sludge. Furthermore, the release of the HMs of indigenous treated/non-treated sludge when added to studied soils was tested during 24 h desorption experiment using (3mM) CaCl_2 . In addition, the studied soils were used alone- as a control sample- to examine the release of soil indigenous HMs under the same conditions. These analyses demonstrated that all HMs content was resident in the sludge -solid phase since all HM concentrations were high in the solid phase, and no significant levels of these metals were present in the organic - DOCs (Table 2). The descending order of the average total metal contents of the digestible sludge extract was $\text{Fe} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Co} > \text{As} > \text{Cd}$. Also from the desorption experiment, no significant levels of HMs were measured in the soil-aqueous phase under natural conditions (CaCl_2 extractant) which represent somewhat the safety use of this sludge in soils under natural conditions (data not shown). Our data were in agreement with many Researchers which reported that metals added to soils as constituent of biosolids are less phytoavailable than metal salt added to the soil (Brown *et al.*, 1998; Bell *et al.*, 1991; Mahler *et al.*, 1987). Further researches are needed to confirm such relation under different soil conditions.

Table 5: Comparison of percent changing of K_d values between Cd and Cu as affected by organic treatments for the three studied soils.

Organic source	Cd	Cu
	Changing K_d %	
Clay		
Clover	-73.24	-97.64
Tr. Clover	+53.57	+15.63
Sludge	-44.91	-93.43
Tr. Sludge	+60.03	+11.53
Calcareous		
Clover	-73.36	-96.94
Tr. Clover	+6.29	+4.88
Sludge	-49.14	-90.2
Tr. Sludge	+21.21	+12.5
Sandy		
Clover	-62.31	-95.65
Tr. Clover	+51.93	+91.38
Sludge	+64.93	-87.63
Tr. Sludge	+258.20	+95.17

(-), decreasing; (+), increasing; Tr., treated (DOC. removed)

CONCLUSIONS

The addition of the clover and sludge significantly decreased the K_d values of Cd and Cu for the studied soils, except for sandy soil for the sludge treatment with Cd. This decrease of metals sorption can be referred to the presence of dissolved organic carbon derived from the sludge and clover organics. Such effect was more pronounced for Cu than for Cd as expressed by the percentage of changing K_d value; since it was more negativity (K_d decreased) for Cu than for Cd. When DOC was removed from the clover and sludge, sorption of Cd and Cu was reflected to increase, and this was more pronounced for Cd than for Cu for most cases as expressed by the percentage of changing K_d value since it was more positivity (K_d increased) for Cd than for Cu except for treated clover in sandy soil. Cd and Cu can offer different degrees for binding sites of organics depending on components-molecular mass of these organics. No significant levels of HMs released from their resident sites of the sludge treating studied soils to soil- aqueous-phase. The treated organics (DOC removed clover and sludge) can be utilized as cheap immobilizing agents for heavy metals such as Cd and Cu in contaminated sites.

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الملخص العربي

تثبيت العناصر الثقيلة في مواقع التلوث باستخدام مواد عضوية طبيعية

محمد لطفى محرم¹، طارق محمد عمر²، هشام محمد جابر³

¹المركز الإقليمي للأغذية والأعلاف- مركز البحوث الزراعية - الإسكندرية

²المركز الإقليمي للأغذية والأعلاف- مركز البحوث الزراعية - القاهرة

³كلية الزراعة - جامعة الإسكندرية - الإسكندرية

أجريت هذه الدراسة لتقييم استخدام بعض مصادر المواد العضوية مثل البرسيم والحماة ، والتي يمكن أن تستخدم في تثبيت العناصر الثقيلة في المواقع الملوثة والتي تستخدم كمعاملات في بعض الأراضي الزراعية. ونتيجة لأن هذه المواد العضوية عبارة عن مواد غير متجانسة التركيب حيث أنها تحتوي على مركبات صلبة وذائبة ، لذا تم إزالة المواد العضوية الذائبة (DOC) من البرسيم والحماة ، والتي تم تسميتها بالمواد العضوية المعدلة، (عن طريق الغسيل عدة مرات بالماء المقطر) وذلك لتقليل التأثير المحتمل لهذه المواد DOC على حركة العناصر الثقيلة الملوثة بالتربة.

لتحقيق هذا الهدف تم إجراء تجارب الامصاص في نظام مغلق (batch system) لبيان تأثير إضافة هذه المواد العضوية سواء المعاملة أو العادية على سلوك كل من الكاديوم والنحاس على ثلاث أنواع من الأراضي المختلفة. أوضحت النتائج أن إضافة المواد العضوية الغير معدلة سواء البرسيم أو الحماة أدى إلى زيادة معنوية في حركة العناصر الثقيلة في الأراضي الملوثة في معظم الحالات (معبرا عنها بثابت معامل التوزيع K_d المحسوب من معادلة فريندلخ) وهذه الزيادة كانت تعزى إلى وجود DOC المتحلل من هذه المواد العضوية ، وهذا التحرر كان أكثر وضوحا لعنصر النحاس عن الكاديوم. على النقيض فعندما عوملت الأراضي تحت الدراسة بالمواد العضوية المعدلة (المنزوع منها المواد العضوية الذائبة) أدى إلى زيادة قدرة هذه الأراضي على حجز الكاديوم والنحاس واعتمدت على كل من نوع المادة العضوية والمعدن والتربة. أيضا تم ملاحظة أن كل من الكاديوم والنحاس اظهرا درجات متفاوتة للارتباط بهذه المواد العضوية اعتمادا على التركيب الجزيئي لهذه المواد العضوية.

أيضا في هذه الدراسة تم قياس المحتوى الكلي والذائب لبعض العناصر الثقيلة الموجودة في البرسيم والحماة، ثم تم عمل تجارب لاختبار تحرر هذه العناصر من الحماة إلى الطور المائي للأراضي تحت الدراسة المعاملة بها وأظهرت النتائج أنه لم يتم حدوث تحرر ملحوظ لهذه العناصر من الحماة إلى الطور المائي للتربة.

النتائج النهائية أوضحت أن هذه المواد العضوية المستخدمة والمتوافرة رخيصة السعر يمكن أن تستخدم كمواد مثبتة للعناصر الثقيلة في المواقع الملوثة بهذه العناصر وتحولها إلى صورة أقل صلاحية لامتصاص النبات وبالتالي يمكن أن تقلل من مخاطر وصول هذه العناصر الضارة إلى سلسلة غذاء الإنسان والحيوان.