

## **Distribution of Different Fractions of Heavy Metals in Desert Sandy Soil Amended with Composted Sewage Sludge**

**Eid Morsy Khaled**

*Department of Soil Science, Faculty of Agriculture, Ain Shams University,  
P.O.Box: 68 Hadayk Shobra, 11241 Cairo, Egypt*

### **Abstract**

An experiment was conducted to assess different fractions and surface accumulation of Zn, Cu, Pb, and Ni in desert sandy soil amended with two rates of composted sewage sludge (20 and 40 g.kg<sup>-1</sup>) were applied to the surface of soil columns. A sequential extraction method was used to determine the soil fractions and surface accumulation of Zn, Cu, Pb, and Ni in treated sandy soil. Both doses of sludge added to soil resulted in a marked increase in the total amount of studied metals. Heavy metals accumulation were found in the surface 5 cm of the treated soil with maximum amount at a sludge rate of 40g.kg<sup>-1</sup> where Zn>Cu>Pb>Ni. Most movement and amount of Zn, Pb, and Ni recovered from soil were predominantly limited to a depth of 15 cm while reached to 25 cm for Cu. At soil depth lower than 25 cm, total values of heavy metals became equal to those of untreated soil sample. The water-soluble fraction of metals were relatively small comparing to the total soil content. Extractable fraction of organically bound Cu was high compared to the other elements. The amount of metals extracted by DTPA extraction followed the same pattern exhibited by the total amounts. Data revealed that the bulk of heavy metals accumulated in the top 15 cm soil depth. Little if any movement of metals had occurred below that depth. Results showed also that more than 90% Ni, Pb, Zn, and 78% Cu, of corresponding total DTPA extractable metals from the whole soil column, were readily extracted by DTPA from the surface 15 cm soil.

**Key Words:** Sandy Soil, Sewage Sludge, Heavy Metals, Distribution, Fractionation

### **Introduction**

Sewage sludge has been utilized as a source of plant nutrients and as a soil amendment for many years. Land application of sewage sludge continues to be a major

environment issue. Application of sludge to agriculture lands based on the content of heavy metals and toxic organics. One of the problems associated with land application has been the presence of considerable concentrations of heavy metals, which are considered to be harmful to plant or animal health. This is especially true when sludge that include industrial contaminants are used (Williams et al, 1985). Walker (1989) indicated that even for "low contaminat" sludge, heavy metals content could be the limiting factor in a sludge application to agricultural land. Over the past decade, a great deal of attention has been directed towards problems of soil pollution involving the accumulation of excess levels from both essential micronutrient and heavy metals. Sludge is rich in organic compounds, and its application to soil is likely to improve fertility (Giusquiani et al, 1988 and 1992) even though it may increase the level of potentially harmful trace metals in the soil (Williams et al, 1980). Depending on origin and composition, however, sludge may contain variable amounts of toxic metals as well as beneficial nutrients. The presence of toxic metals in sewage sludge can affect plants, ground water or human health by contamination of food chain (Lamy et al, 1993).

Studies of ions or salt movement in soil have been focused, primarily, on such salts as the nitrates and chlorides, which exist as soluble salts and move readily in the soil solution. With greater emphasis being placed on sewage sludge and its use in agriculture, concern has recently been shown for the possible movement of heavy metals in the soil (Williams et al, 1980). The movement of sludge-borne heavy metals beyond the zone of incorporation is of concern. Mullins et al (1982) could not detect movement of DTPA-extractable Cu or Zn below 23 cm in a silty clay soil. After 8 yr. of applying upto  $225 \text{ Mg ha}^{-1}\text{yr}^{-1}$  of sewage sludge to a loamy soil, Williams et al (1987) found that 4 M  $\text{HNO}_3$ -extractable Zn, Cu, Cd, and Ni had moved 5 to 10 cm below the zone of incorporation. Movement of these metals below 30 cm was not detected. Andersson and Nilsson (1972) suggested that heavy metals supplied with sewage sludge ( $84 \text{ Mg ha}^{-1}$ ) over a 2-yr. period remained in the surface 20 cm of soil.

The relative immobility of metals added to the soil reflects the various chemical reactions that take place in the soil. Riffaldi and Levi-Minzi (1975), Petruzelli et al (1978), Jones and Jarvis (1981), and Emmerich et al (1982) have reported that many metals are absorbed or complexes by organic matter. In addition, adsorptions on hydrous oxides of iron and cation exchange reactions are important modes of metal immobility (White and Chaney, 1980; Chubin and Street, 1981). Moreover, Berrow and Webber (1972), Bloomfield and Pruden (1975) and Lagerwerff et al (1976) reported that numerous immobile forms of a given metal might occur in sludge. Some of these, as listed by Stover et al (1976) are the exchangeable, sorbed, organic-bound forms, carbonates and sulfides. In most all cases, the metals are in an immobile form at the time they are added to the soil. The objective of the experiment reported here was to further evaluate possible hazards that might arise from additions of high metal content sludge to soil. Therefore, we examine the metals Zn, Cu, Pb and Ni

concentrating on the amounts accumulated in the soil and the movement of these metals within the soil columns. The chemical forms of solid-phase heavy metals in different segments of sludge treated soil were measured using sequential extractions. DTPA-extractable metals were determined as a function of soil depth.

### **Materials and methods**

#### **Soil samples**

Surface soil samples (0-30 cm) were collected from a site called eastern Cerabium region 2 at about one kilometer from Ismailia-Suez Canal. This soil is Typic Torripsamments. Soil samples were air dried and ground to pass through a 2-mm sieve. Subsamples of the soil were analyzed and the characterization of the soil is given in Table 1. Methods were as follow: pH 1:2.5 in water (McLean, 1982), cation exchange capacity (Rhoades, 1982), organic matter by wet oxidation (Nelson and Sommers, 1982), soil particle size distribution, calcium carbonate content and total salts in the soil past extraction (Richards, 1954), total Zn, Cu, Pb and Ni by atomic absorption spectrophotometer after nitric-perchloric digestion (Korcak and Fanning, 1978), and the DTPA used a soil to solution ratio of 1 to 2 and a reaction time 2 h. (Lindsay and Norvell, 1978).

#### **Sewage sludge**

Aerobically digested and semidried sewage sludge was collected from Abou-Rawash sewage treatment plant in Giza Governorate, Egypt. This sludge was mixed with city waste in a 1:1 ratio (wet weight basis) and placed in a 0.25 m<sup>3</sup> wood box to composted for about 90 days as described by Abou-Seeda et al. (1996). Then, sludge was air dried, crushed and sieved through a 2 mm screen and was used as such in this study. The analyses of sewage sludge are given in Table 2. Total nitrogen was determined by semi-micro-Kjeldahl as given by Bremmer and Mulvaney (1982). The other properties were determined using the same methods were used for soil analyses.

#### **Column experiment**

The columns were constructed from preweighed polyvinylchloride pipes (4 cm internal diameter and 40 cm length) with an end cap drilled for an outlet, which was covered with a layer of pre-washed cheesecloth to prevent the escape of soil particles. Five hander grams soil sample were poured into each column through a funnel with a plastic tube extension to reach the bottom. This was gradually raised to minimize particle segregation as filling proceeded (Bellini et al 1996). The column was vibrated during packing where the final bulk density was approximately 1.3 g cm<sup>-3</sup>. The depth of the soil was 30 cm, and each treatment was duplicated. Each packed column was wetted from the bottom with deionized water prior to leaching the column with 100 ml solution containing 0.02 M NaCl. After the initial leaching the sewage sludge was

mixed with 20 g soil sample and added to the surface of each column to equilibrated for 4 weeks at water field capacity of soil. Two rates of sewage sludge were considered in this experiment, which correspond to 20 and 40 g.kg<sup>-1</sup> soil. After the equilibrium time, each column was divided into 6 segments of 0 to 5, 5 to 10, 10 to 15, 15 to 20, 20 to 25, and 25 to 30 cm. The soil samples were air dried, ground and analyzed for total and DTPA extractable Zn, Cu, Pb, and Ni. Fractionation of metals in soil samples were made by the method of Rauret et al (1989) as given by Ramos et al (1994) into five components: Water soluble, exchangeable, carbonates, associated with Fe-Mn oxides and with organic matter. Heavy metals content of the five fractions were measured by atomic absorption spectrophotometer. The amount of extracted metals in each fraction, as a percent of total metal content, was calculated. The obtained data for each treatment were the average values of duplicate samples taken from each segment of duplicated columns.

### Results and discussion

The soil under consideration has a poor agricultural value, as can be derived from their general characteristics in Table 1. Organic matter content, CEC, DTPA extractable micronutrients are low, while the pH and sand % are high. Total Zn contents are higher than the soil contents of others heavy metals. The sewage sludge used in this study contains 34.7 % of organic carbon and 1.35 % of total nitrogen (Table 2). The sludge contains high amount of total as well as a considerable amount of DTPA-extractable metals. The amounts of metals in sludge was found to be Zn > Cu > Pb > Ni.

Addition of the sludge to surface of the soil resulted in a marked increase in the amount of total Zn, Cu, Pb and Ni at both doses of 20 and 40 g.kg<sup>-1</sup> soil, as given in Figure 1. The increases corresponding, in general, to the rate of sludge addition and to the concentrations of metals presented in the sludge. For each rate of metal application, total amounts were presented (mg/kg soil) as a function of soil depth. Maximum total concentrations of metals were found in the surface layer of soil (0-5 cm) at the highest rate (40 g.kg<sup>-1</sup>) of sludge treatment and were as follow: Zn 185, Cu 140, Pb 80 and Ni 75 mg.kg<sup>-1</sup> soil. Despite a marked increasing of metal concentrations, most amount of metals recovered and their movement in the soil were predominantly limited to a certain soil depth. Values obtained became equal to those of untreated soil samples (Table 1) at the depths lower than 15, and 25 cm for Zn, Pb and Ni, and Cu, respectively. Andersson and Nilsson (1972) found that, after 12 yr. of adding 84 Mg ha<sup>-1</sup> of sludge to soil, heavy metals remained in the surface 20 cm of soil. A low mobility of heavy metals added to soils was shown by a number of workers. McLaren and Crawford (1973) and Williams et al (1980 and 1985) stated that low mobility was due to specific adsorption of the metals.

Distribution of Different Fractions of Heavy Metals in Desert Sandy Soil  
Amended with Composted Sewage Sludge

5

Table 1: Some soil physical and chemical characteristics.

Property	Value
pH (H <sub>2</sub> O)	7.2
EC (ds.m <sup>-1</sup> )	2.2
CaCO <sub>3</sub> (%)	3.5
CEC (cmol.kg <sup>-1</sup> )	2.95
Org. matter (%)	0.25
Sand (%)	90
Silt (%)	6
Clay (%)	4
Texture	Sandy
DTPA-extracted metals (mg.kg <sup>-1</sup> )	
Zn	0.5
Cu	0.2
Pb	0.2
Ni	nd
Total metals content (mg.kg <sup>-1</sup> )	
Zn	98.0
Cu	56.5
Pb	20.0
Ni	52.0

nd: not detected

Table 2: Characterization of the composted sewage sludge

Property	Value
Sewage sludge fraction < 2mm (%)	87.6
pH(H <sub>2</sub> O)	7.1
Org. carbon (%)	34.7
EC (ds.m <sup>-1</sup> )	3.35
Total N (%)	1.35
DTPA-extractable metals (mg.kg <sup>-1</sup> )	
Zn	107.5
Cu	52.6
Pb	21.5
Ni	25.2
Total metals content (mg.kg <sup>-1</sup> )	
Zn	476.5
Cu	352.3
Pb	284.6
Ni	176.5

The chemical forms of solid-phase heavy metal (as a percent of total metal content) in different soil depths are given in Table 3. The water extractable fraction of heavy metals was extremely low compared to the total content. This could be related to the alkalinity of the soil. The exchangeable metal levels ranged between not detected to 2.1% for Zn, 0.2 to 3.4% for Cu, not detected to 2.4% for Pb and not

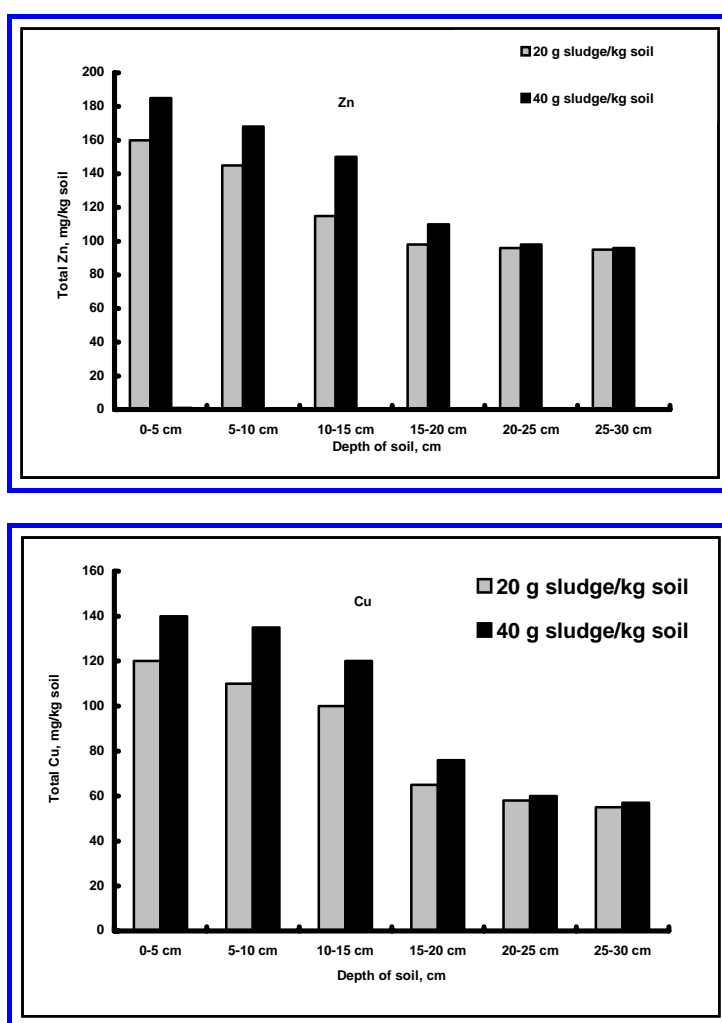


Figure 1: Total amount of Zn, Cu, Pb and Ni (mg/kg) from sewage sludge amended soil as a function of soil depth.

Distribution of Different Fractions of Heavy Metals in Desert Sandy Soil Amended with Composted Sewage Sludge

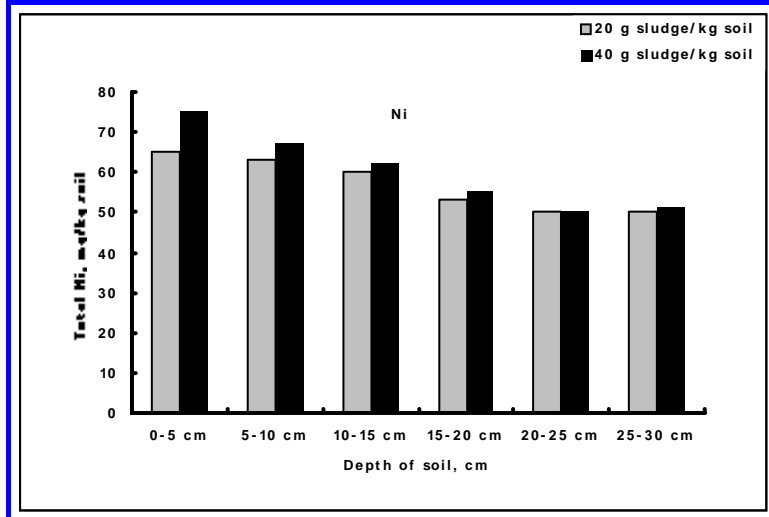
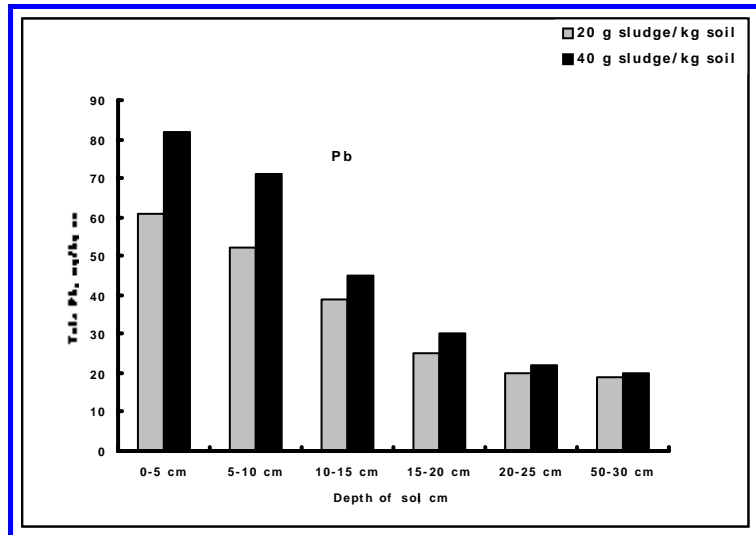


Figure 1: Continued

Table 3: The Chemical forms of solid-phase heavy metal (as a percent of total metal content) in different soil depths.

Form of metal	Depth of soil samples, cm.											
	0-5		5-10		10-15		15-20		20-25		25-30	
	a	b	a	b	a	b	a	b	a	b	a	b
	Zn ( % )											
Water	0.4	0.6	0.2	0.8	0.1	0.1	nd	nd	nd	nd	nd	nd
Exchangeable	1.6	2.1	1.9	1.5	1.4	1.6	0.2	0.2	nd	nd	nd	nd
Carbonates	12.6	14.4	14.6	15.0	9.4	9.9	2.5	2.9	1.2	1.5	0.6	0.5
Fe/Mn oxides	24.3	26.8	25.8	28.4	21.1	24.3	4.6	5.3	2.6	3.6	1.2	1.0
Org. matter	6.3	8.5	7.2	9.7	4.2	6.3	2.3	3.0	1.3	1.6	nd	nd
	Cu ( % )											
Water	0.6	1.4	0.9	1.2	0.6	0.9	0.5	0.4	0.3	0.2	0.1	0.1
Exchangeable	3.2	3.4	3.0	3.3	2.8	3.2	1.9	2.4	0.9	1.5	0.2	0.3
Carbonates	8.2	12.6	6.0	9.5	7.1	8.5	3.9	4.8	2.3	3.5	1.7	2.2
Fe/Mn oxides	15.9	22.4	18.5	19.0	10.3	14.4	8.5	10.0	4.5	6.0	3.2	4.0
Org. matter	25.4	30.5	32.2	33.0	22.3	25.0	15.6	18.0	7.5	9.0	4.2	5.0
	Pb ( % )											
Water	0.1	0.2	0.2	0.2	0.1	0.2	0.1	nd	nd	nd	nd	nd
Exchangeable	2.0	2.3	2.4	2.3	2.0	1.9	1.2	1.0	nd	nd	nd	nd
Carbonates	2.6	3.4	2.5	4.0	1.5	1.4	0.8	1.5	nd	nd	nd	nd
Fe/Mn oxides	5.6	6.0	3.8	4.0	4.2	6.0	2.3	3.2	nd	nd	nd	nd
Org. matter	4.3	6.5	4.4	5.2	3.4	4.7	2.4	2.8	1.0	1.5	nd	nd
	Ni ( % )											
Water	0.4	0.5	0.6	0.8	0.6	0.7	nd	nd	nd	nd	nd	nd
Exchangeable	2.2	3.4	3.0	3.3	2.0	3.2	1.9	nd	nd	nd	nd	nd
Carbonates	5.2	8.6	6.0	9.4	5.1	8.5	3.9	4.8	nd	nd	nd	nd
Fe/Mn oxides	13.9	20.4	14.5	19.0	9.3	14.4	6.5	7.0	nd	nd	nd	nd
Org. matter	15.4	20.5	22.2	26.0	15.3	21.0	9.6	11.0	2.5	3.0	nd	nd

a: rate of added sludge = 20 g.kg<sup>-1</sup> soil

nd= not detected

b: rate of added sludge = 40 g.kg<sup>-1</sup> soil



detected to 3.4% for Ni. The movement of metals in the various chemical fractions was dependent on the total metal content of the soil samples at different soil depths. The relative immobility of the metals added to the soil in sludge is a reflection of the chemical reactions that occur in the soil (Williams et al, 1980 and 1987). The amount of Zn in each fraction followed the order Fe-Mn oxides > carbonates > organic > exchangeable > water-soluble (Table 3). This sequence for Pb was Fe-Mn oxides > organic > carbonate > exchangeable > water-soluble. Copper and nickel has a different pattern with the organic fraction dominating the distribution. The amount of Cu and Ni in each fraction followed the order organic > Fe-Mn oxides > carbonates > exchangeable > water-soluble. A similar distribution pattern was observed for Cu and Zn by Ramos et al (1994). The high amount of Zn and Pb associated with Fe-Mn oxides may include metals present in other poorly crystalline compounds. Regarding to Zn, several other workers have found Zn to be highly associated with Fe-Mn oxides and calcium carbonate (Kuo et al, 1983; Ramos et al, 1994). The presence of heavy metals in the carbonate fraction might indicate a pH suitable for metal precipitation. Moreover, calcium carbonate may act as a strong absorbent for heavy metals and could complex as double salts like  $\text{CaCO}_3 \cdot \text{MCO}_3$  (Ramos et al, 1994).

The preference of Cu for organic matter is supported by the high stability of Cu complexes with organic components (Spevackova and Kucera, 1989; Pardo et al, 1990). Copper forms relatively strong organic-metal complexes, which can be the reason for slightly movement of the copper in the soil.

Using DTPA extracting to measure movement and availability of the metals in the soil column, results showed that the bulk of the added metals remained in the top 20 cm of soil (Figure 2). Data revealed that the amounts of metals extracted by DTPA solution at sludge rates of 20 and 40  $\text{g.kg}^{-1}$  soil were generally decreased with increasing soil depth. It should be noted that the metals availability as extracted by DTPA in the soil is correlated with rate of the added sludge. Shuman (1986) mentioned that, the better extraction is DTPA since it produced correlation between the plant metal content and DTPA extractable metal. DTPA extracted Zn, Cu, Pb and Ni followed the same pattern exhibited by total amounts. Most of extractable metals were obtained from surface soil (0-15 cm). From the surface 15 cm of sludge treated soil, DTPA was able to extract more than 90 % Zn, Pb and Ni and 78 % Cu, of corresponding total DTPA extractable metals from the whole soil column, as given in Table 4.

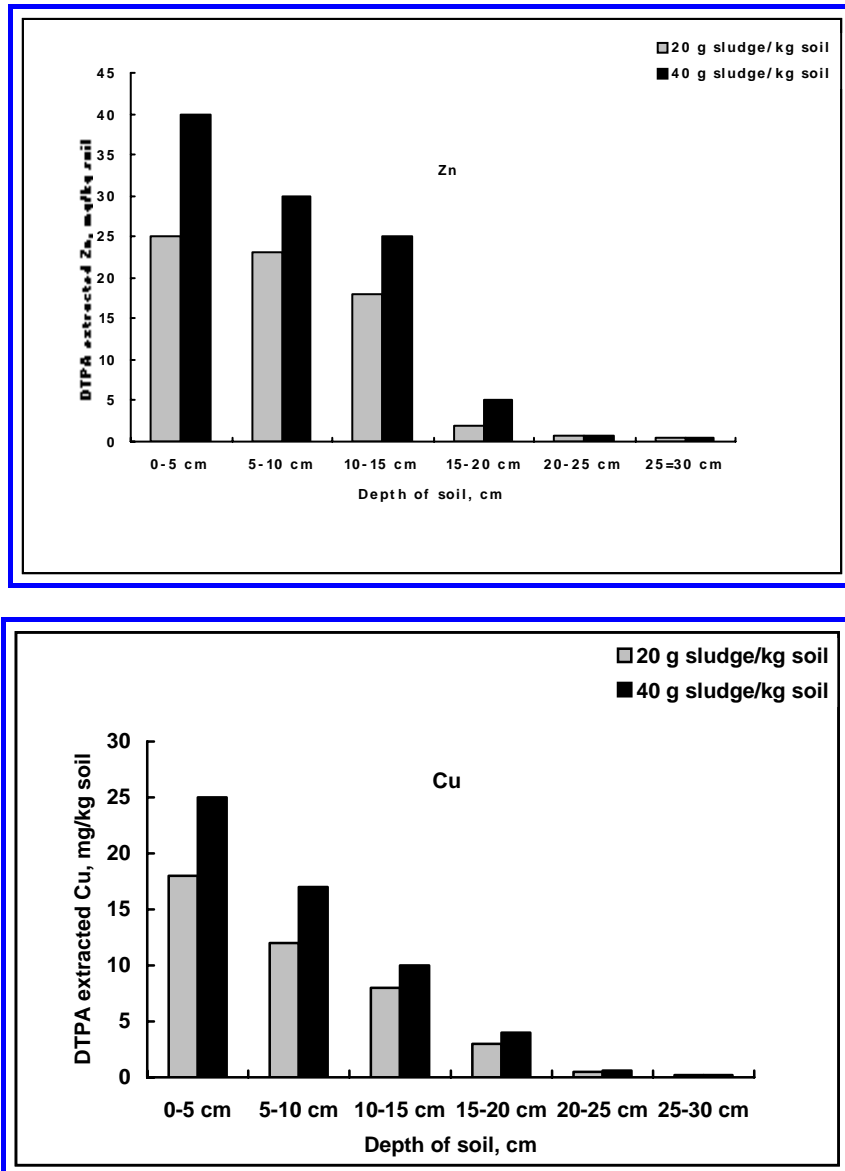


Figure 2: DTPA extracted Zn, Cu, Pb and Ni (mg/kg soil) from sewage sludge amended soil as a function of soil depth.

Distribution of Different Fractions of Heavy Metals in Desert Sandy Soil Amended with Composted Sewage Sludge

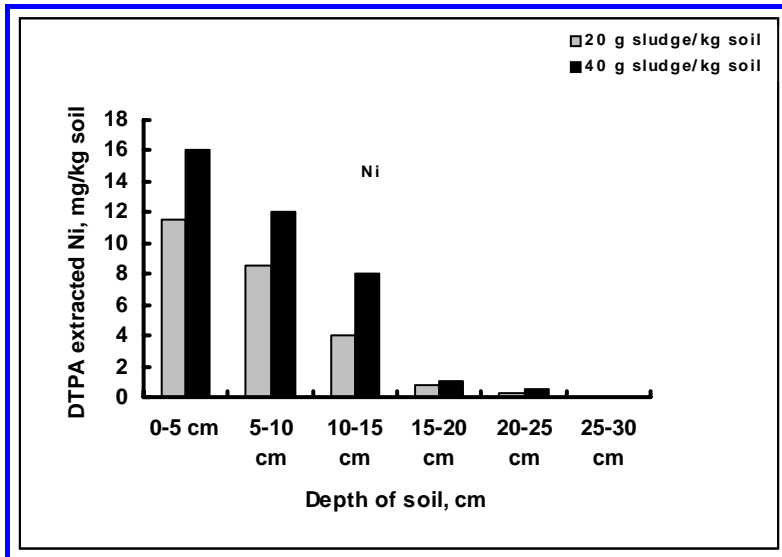
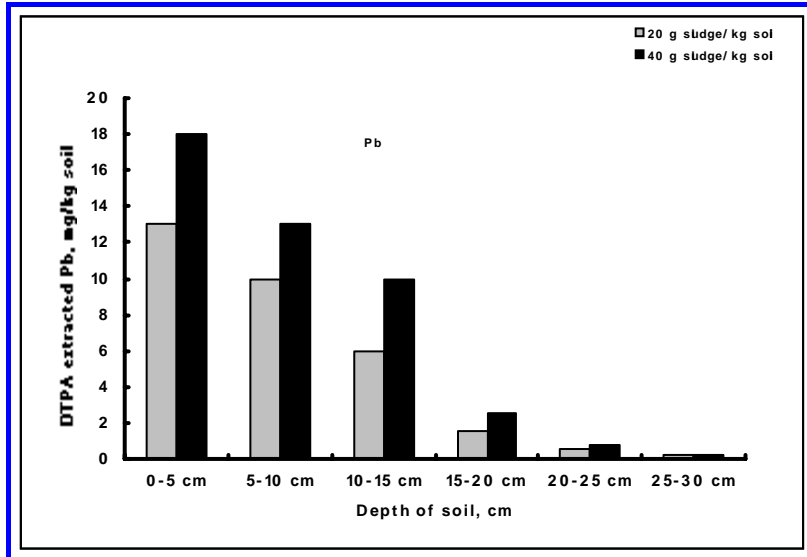


Figure 2: Continued

Table 4: DTPA-extracted metals from surface (0-15) and subsurface (15-30) soil column as percent of total DTPA amount extracted

Depth (cm)	Zn		Cu		Pb		Ni	
	a	b	a	b	a	b	a	b
0-15	97.0	96.3	78.2	82.5	94.5	93.6	91.5	92.0
15-30	3.0	3.7	21.8	17.5	5.5	6.4	8.5	8.0

a: rate of added sludge = 20 g.kg<sup>-1</sup> soil

b: rate of added sludge = 40 g.kg<sup>-1</sup> soil

An examination of the data showed that little if any movement had occurred below 20 cm, except the Cu which can moved upto 25 cm depth. These results indicated that the chemical behavior of Cu, and Ni in the soil might be similar. This probably due to that, organic material can influence the solubility of Cu and Ni by forming organic complexes. An increase in water-soluble organic form of metal is generally associated with an increase of its availability and a heightened movement of metal in the soil (Williams et al, 1980). Our data showed this to be only true for the Cu as can be observed in Table 4, where about 20 % of DTPA extracted Cu was obtained at soil depth lower than 15 cm. While at the corresponding soil depth, DTPA solution was extracted 3.4, 6.0, and 8.2 % of Zn, Pb, and Ni, respectively. The high amount of Cu extracted from lower depth may thus be explained by the high affinity of soluble organic fraction particularly fulvic acid toward Cu than other metals. Similar observation by Senesi et al (1985) proved that soil fulvic acid showed a high affinity for Cu availability.

It can be concluded that, a wide variation in the concentrations of heavy metals extracted from the surface 15 cm of sewage sludge treated soil compared to that extracted from untreated soil, indicating apparent contamination to have taken place. Apparently, marked contamination of the surface soil with heavy metals was also suggested by the large increase in total metals concentration found compared to that amounts obtained from the lower soil depth. Mobility of heavy metals were followed the order Cu > Ni > Pb > Zn. The amount of Zn in each fraction followed the order Fe-Mn oxides > carbonates > organic > exchangeable > water-soluble. This sequence for Pb was Fe-Mn oxides > organic > carbonates > exchangeable > water-soluble. While the amount of Cu and Ni followed the order: organic > Fe-Mn oxides > carbonates > exchangeable > water-soluble. The heavy metals added with sludge were already present in the soil in amounts that would be toxic if completely soluble. However, most of the metals originally present in the soil under study are held in forms that are relatively immobile, and unavailable to plants, and the added metals will also tend to become immobilized.

### References

- Abou-Seeda, M.; A. Khater and E. M. Khaled (1996).** Use of sewage sludge for sustainable agriculture and pollution preservation. 1. Composting of sewage sludge. *J. Agric.Sci. Mansoura Univ.*, 21:4179- 4193.
- Andersson, A. and K.O. Nilsson (1972).** Enrichment of trace elements from sewage sludge fertilizers in soils and plants. *Am. Biol.* 1:176-179.
- Bellini, G.; M. E. Summer; D. E. Radcliffe and N. P. Qafoku (1996).** Anion transport through columns of highly weathered acid soil: Adsorption and retardation. *Soil Sci. Soc. Am. J.* 60:132-137.
- Berrow, J. L. and J. Webber (1972).** Trace elements in sewage sludge. *J. Sci. Food Agric.* 23:93-100.
- Bloomfield, C. and G. Pruden (1975).** The effect of aerobic and anaerobic incubation on the extractability of heavy metals in digested sewage sludge. *Environ. Pollut.* 8: 217-232.
- Bremmer, J. M. and C. S. Mulvaney (1982).** Nitrogen- Total. In: *Methods of soil analysis part 2.* Agronomy 9:595-624, Page, A. L. (ed.). Am. Soc. Agron., Madison, Wis.
- Chubin, R. G. and J. J. Street (1981).** Adsorption of cadmium on soil constituents in the presence of complexing ligands. *J. Environ. Qual.* 10:225-228.
- Emmerich, W. E.; L. J. Lund; A. L. Page and A. C. Change (1982).** Predicted solution phase forms of heavy metals in sewage sludge treated soils. *J. Environ. Qual.* 11:182-186.
- Giusquiani, P. L.; C. Marucchini and M. Businelli (1988).** Chemical properties of soils amended with compost of urban waste. *Plant Soil* 109:73-78.
- Giusquiani, P. L.; G. Gigliotti and D. Businelli (1992).** Mobility of heavy metals in urban waste- amended soils. *J. Environ. Qual.* 21:330-335.
- Jones, L. H. P. and S. C. Jarvis (1981).** The fate of heavy metals. In: *The chemistry of soil processes.* PP. 593-620, Greenland, D. J. and M. H. B. Hayes (eds.), Wiley New York.

- Korack, R. F. and D. S. Fanning (1978).** Extractability of cadmium, copper, nickel, and zinc by double acid versus DTPA and plant content at excessive soil levels. *J. Environ. Qual.* 7:506-512.
- Kuo, S.; P. E. Heilman and A. S. Baker (1983).** Distribution and forms of copper, zinc cadmium, iron, and manganese in soils near a copper smelter. *Soil Sci.* 135:101-109.
- Lagerwerff, J. V.; G. T. Biersdorf and D. L. Brower (1976).** Retention of metals in sewage sludge: 1. Constituent heavy metals. *J. Environ. Qual.* 5:19-23.
- Lamy, I.; S. Bourgeois and A. Bermond (1993).** Soil cadmium mobility as a consequence of sewage sludge disposal. *J. Environ. Qual.* 22:731-737.
- Lindsay, W. L. and W. A. Norvell (1978).** Development of a DTPA soil test for Zinc, iron, manganese, and copper. *Soil Sci. Soc. Am. J.* 4:421-428.
- McLaren, R. G., and D. V. Crawford (1973).** Studies on soil copper. 2. The specific adsorption of copper by soil. *J. Soil Sci.* 24:443-452.
- McLean, E. O. (1982).** Soil pH and lime requirement. In: *Methods of soil analysis part 2. Agronomy 9:199-224*, Page, A. L. (ed.). Am. Soc. Agron., Madison, Wis.
- Mullins, G. L.; D. C. Martens; S. W. Gettier and W. P. Miller (1982).** Forms and availability of copper and zinc in a Rhodic Paleudult following long-term  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  applications. *J. Environ. Qual.* 11:573-577.
- Nelson, D. W. and L. E. Sommers (1982).** Total carbon, organic carbon, and organic matter In: *Methods of soil analysis part 2. Agronomy 9:539-579*, Page, A. L. (ed.). Am. Soc. Agron., Madison, Wis.
- Pardo, R.; E. Barrado; L. Perez and M. Vega (1990).** Determination and speciation of heavy metals in sediments of the Pisuerga river. *Wat. Res.* 24:373-379.
- Petruzelli, G.; G. Guide and L. Lubrano (1978).** Organic matter as an influencing factor on copper and cadmium adsorption by soils. *Water, Air, Soil Pollut.* 9:263-269.
- Ramos, L.; L. M. Hernandez and M. J. Gonzalez (1994).** Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Donana National Park. *J. Environ. Qual.* 23:50-57.

- Rauret, G.; R. Rubio; J. F. Lopez-Sanchez and E. Casassas (1989).** Specific procedure for metal solid speciation in heavily polluted river sediments. *Int. J. Environ. Anal. Chem.* 35:89-100.
- Rhoades, J. D. (1982).** Cation exchange capacity. In: *Methods of soil analysis part 2. Agronomy* 9:149-157, Page, A. L. (ed.). Am. Soc. Agron., Madison, Wis.
- Richards, L. A. (1954).** Diagnosis and improvement of saline and alkaline soils. U. S. Dept. Agron., *Agric. Handbook* 9:83-126.
- Riffaldi, R. and R. Levi-Minzi (1975).** Adsorption and desorption of cadmium on humic acid fractions of soils. *Water, Air, Soil Pollut.* 5:179-184.
- Senesi, N.; D. F. Bocian and G. Sposito (1985).** Electron spin resonance investigation of copper II complexation by soil fulvic acid. *Soil Sci. Soc. Am. J.* 49:114-119.
- Shuman, L. M. (1986).** Effect of liming on the distribution of manganese, copper, iron, and zinc among soil fractions. *Soil Sci. Soc. Am. J.* 50:1236-1240.
- Spevackova, V. and J. Kucera (1989).** Trace element speciation in contaminated soils studied by atomic absorption spectrometry and neutron activation analysis. *Int. J. Environ. Anal. Chem.* 35:241-251.
- Stover, R. C.; L. E. Sommers and D. J. Silveira (1976).** Evaluation of metals in waste water sludge. *J. Water Pollut. Control Fed.* 48:2165-2175.
- Walker, J. M. (1989).** Assessment of sludge regulation assumptions: A framework for analysis. *Biocycle*, 30:71- 83.
- White, M.C. and R., L. Chaney (1980).** Zinc, cadmium and manganese uptake by soybean from two zinc and cadmium amended coastal plain soils. *Soil Sci. Soc. Am. J.* 44:308-313.
- Williams, D.E; J. Vlamis; A. H. Pukite and J. E. Corey (1980).** Trace element accumulation, movement, and distribution in the soil profile from massive applications of sewage sludge. *Soil Sci.* 129:119-132.
- Williams, D.E; J. Vlamis; A. H. Pukite and J. E. Corey (1985).** Metal movement in sludge-treated soils after six years of sludge addition: 2. Nickel, cobalt, iron, manganese, chromium, and mercury. *Soil Sci.* 140:120-125.
- Williams, D.E; J. Vlamis; A. H. Pukite and J. E. Corey (1987).** Metal movement in sludge – amended soil: A nine-year study. *Soil Sci.* 143:124-131.