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Mobilization of Pb, Zn, Cu and Cd, in Polluted Soil

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Abstract: Effect of chicken manure extract (CHCME), cow manure extract (COWME) and sewage effluent (SE) on mobilization of Pb, Zn, Cu and Cd, a sandy soil from central region of Saudi Arabia, were studied in columns experiment. All solutions were able to mobilize, only, very small portions (less than 0.55%) of total amount of Pb previously added to soil. The affinity of Pb to soil is higher than the ability of organic and inorganic ligands of CHCME, COWME and SE to form soluble complexes with soil Pb. Although the amounts of soil Zn mobilized in SE (0.16%), COWME (0.55%) and CHCME (3.2%), were relatively higher than those of Pb, Zn ions prefer association with soil solid phase rather than complexing with solution dissolved organic ligands. However, EDTA was able to mobilize higher percentages of soil Pb (49%) and Zn (24%). These results mean that, formation of stable chelates were critical for solubilization of solid phase Pb and Zn. Although both SE and COWME had very limited efficiency in mobilizing soil Cu (0.15 and 0.37%, respectively), CHCME had markedly higher one (25%). The dissolved organic ligands of CHCME prove high efficiency, identical to that of EDTA (25%), in forming soluble Cu complexes. Unlike Pb, Zn and to a lesser degree Cu, soil Cd was ready to be mobilized in all leaching solutions, at varied quantities, H₂O (7.7%), COWME (10.4%), SE (24%), CHCME (43%) and EDTA (84%). These results verified that soil Cd is distributed among different forms; water soluble, exchangeable and specifically adsorbed on solid phase. Soil Cd tends to be more mobile and available to plant, than Pb, Cu and Zn. Mobilization of soil Cd, Cu, Zn and to a lesser degree Pb, were enhanced by CHCME rather than by COWME and SE.

Key words: Polluted soil, mobilization of heavy metals, chicken manure extract, cow manure extract, sewage effluent

INTRODUCTION

Various forms of heavy metals, when added to soils, slowly redistribute among their solid-phase components^[1,2]. Once in soil, some of these metals would be persistent because of their fairly immobile nature. Other metals, however, would be more mobile; therefore, the potential of transfer either through the soil profile down to the ground water aquifer or via plant-root uptake (i.e., bioavailable) is likely^[3]. Environmental hazards derived from heavy metals are closely linked to metal mobility, thus to the concentrations of the metals in the soil solution. The mobility of heavy metals in terms of leachability depends not only on the total concentration in soil but also on soil properties and environmental factors^[4]. Soil containing much organic and mineral colloidal material, can sorbs and immobilize these metals to a greater extent than soil poor in these reactive

materials. Thus, silicates, carbonates, phosphates, oxides and organic matter can all contribute to metal retention. Among the soil environmental factors, pH and organic matter, are known to affect the trace metal transfer between soil phases^[5-9], thus metal solubility in many soils^[10,11]. Organic substances are essentially a mixture of compounds with different molecular weights^[12]. Complexes with monodentate ligands are usually less stable than those with multidentate ligands; therefore, large soil organic molecules are more important for metal retention than low molecular weight organics. However, at higher soil pH levels, dissolved organics can increase the solubility of metal ions by formation of soluble organometallic complexes, which compete with the solid phases for metal ions^[7,8,13]. Soluble organic matter (fulvic acid), which can suppress heavy metal adsorption on Fe and Al oxides and silicate minerals at high pH^[14,15], generally has a sufficiently strong affinity for metals such

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as Cu, Ni, Hg and Pb, that it promotes dissolution of these metals from adsorption sites on clay minerals.

Dissolved organic matter in poultry litter could contribute effective organic ligands to form complexes with heavy metals in soil^[16,17]. The soluble complexes with heavy metals can be transported downward and possibly deteriorate groundwater quality. Not only poultry litter, but also sewage sludge and forest litter can release a large amount of soluble organic ligands^[18]. Sposito *et al.*^[19] demonstrated that the water soluble fraction of sewage sludge was similar to fulvic acid fraction in natural soil organic matter, which was especially reactive to trace metal cations. However, Boyle and Fuller^[20] found that Zn leaching through soil columns was enhanced by elevating the dissolved organic carbon (DOC). Lamy *et al.*^[21] concluded that mobility of Cd was enhanced by an increase in soluble organic matter. Dowdy and Volk^[22] suggested that the movement of heavy metals in soils would occur in sandy, acid, low-organic matter soil, subjected to heavy rainfall or irrigation. Schirado *et al.*^[23] observed that Zn, Cd and Ni migrated from the cultivated soil layer into deeper ones in a silt loam soil due to high annual rainfall.

Agricultural soils are regularly amended with fertilizers and many also receive organic manure. Poultry and cattle manure have been used as soil amendments for decades to enhance soil fertility^[24]. Although organic manure rarely contains high levels of potentially harmful metals such as Pb and Cd^[9], land disposal of organic manures may alter metal status in soil by affecting metal solubility^[25]. Also, sewage effluent has been used in irrigation of agricultural soils adjacent to cities, particularly in arid and semi arid regions. Since cultivated soils in the Central Region of Saudi Arabia are characterized by low content of both organic and mineral colloids^[26,27], annual application of organic manure is needed to improve their properties. Also, due to shortages in fresh water, the reuse of treated sewage effluent in cultivation is increasing. The present investigation intended to study the effect of chicken manure extract (CHCME), cow manure extract (COWME) and Sewage Effluent (SE) in mobilization of Pb, Zn, Cu and Cd, in soil previously polluted with these metals. Since complexation with solid phase is the most probable mechanism controlling metal mobility in soil, EDTA (as one of the strongest synthetic chelating agents) was used for comparison. Its chelating ability is usually much larger than the naturally occurring ligands^[28]. Distilled water was used as a blank control.

MATERIALS AND METHODS

Soil

Soil characteristics: A surface (30 cm) sandy soil from the Central Region of Saudi Arabia (Al-Qassim area) was used in the present study. The soil has high pH value of 7.8, low clay content of (3.2%), low CEC value ($1.5 \text{ C mol}_c \text{ kg}^{-1}$), low organic matter (0.3%) and total carbonate contents (3.1%). The soil had low contents of total Pb, Zn, Cu and Cd (Table 1).

Soil preparation: The soil sample used in this study was polluted with Pb, Zn, Cu and Cd solution. A solution of 5 L containing total soluble amounts of 4000, 8000, 2000 and 400 mg Pb, Zn, Cu and Cd, was prepared using analytical grade reagents of PbCl_2 , ZnCl_2 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CdCl}_2 \cdot 2.5 \text{ H}_2\text{O}$, respectively. The solution was added to 20 kg of a soil sample, i.e., the soil sample received 400, 200, 100 and 20 mg kg^{-1} Zn, Pb, Cu and Cd, respectively. The added solution was enough to over saturate the soil. The soil was mixed well and left to air dry, then crushed, sieved (2 mm) and kept in plastic jars. Portions of 1890 g of the treated soil sample were packed to a height of 20 cm in 10 PVC columns (has dimensions of 30 cm height and inside diameter of 8.6 cm. The bulk density of the soil was 1.63 g cm^{-3}). No control is included because the soil used in this study contains low contents of total Pb, Zn, Cu and Cd, as extracted by DTPA and EDTA (Table 1).

Leaching solutions: Chicken manure extract (CHCME), cow manure extract (COWME), Sewage Effluent (SE) and $\text{Na}_2\text{-EDTA}$ solution (0.01 M) were used to study the mobilization of Pb, Zn, Cu and Cd, previously added to soil. Both CHCME and COWME were prepared by stirring portions of their solid materials in distilled water, at rate of 50 g L^{-1} (manure: water) for 2 h. Then, the suspension were centrifuged for 10 min at 6500 rpm and filtered. The pH values of the supernatant solutions of CHCME and COWME were 8.82 and 6.45, respectively. The pH value of EDTA solution was acidic (4.7), whereas that of SE was 7.23. The pH of CHCME, COWME and SE were adjusted to a value matching that of the tested soil (7.8), by addition of HCl or NaOH.

The chemical analysis of leaching solutions (Table 2) showed that CHCME had the highest values of both total dissolved solids ($\text{TDS} = 10.07 \text{ dS m}^{-1}$) and dissolved organic carbon, DOC, (51.1 meq L^{-1}). Also, CHCME had the highest Cl^- concentration of 16.8 meq L^{-1} . On the other hand, Ca concentration in the CHCME (1.28 meq L^{-1}) was much lower than that of SE (3.80 meq L^{-1}), but it was higher than that of COWME (0.99 meq L^{-1}).

Table 1: General properties of soil

pH (1:1)	7.80
EC (1:1), (dS m ⁻¹)	2.37
Silt+Clay (%)	6.20
OM (%)	0.30
CEC (C mol, kg ⁻¹)	1.50
Total carbonate content (%)	3.10
Total-Pb (mg kg ⁻¹)	5.75
Total-Zn (mg kg ⁻¹)	13.00
Total-Cu (mg kg ⁻¹)	4.95
Total-Cd (mg kg ⁻¹)	0.05

Table 2: Chemical analysis of extract solutions

Leaching solution	EC (dS m ⁻¹)	Soluble inorganic ions (meq L ⁻¹)		
		Ca	Cl	DOC* (meq L ⁻¹)
COWME	2.03	0.99	9.09	11.1
CHCME	10.07	1.28	16.83	51.1
SE	1.45	3.80	7.65	ND

*Dissolved organic carbon

Leaching process: The three leaching solutions; CHCME, COWME and SE; as well as EDTA and distilled H₂O, were added to the soil columns. Each leaching solution was added to two columns (two replicates) at room temperature of 24±0.5°C. The solutions were ponded at 5 cm above the soil surface and maintained at this level until the end of leaching process. Twenty-five mL aliquots of percolating solution were collected from each column. Except for soil columns treated with sewage effluents, the total volume collected from percolating solution was 625 mL. The collected volume is equal to about one pore volume of the soil. (The pore volume of the soil = 351 cm³ kg⁻¹). The total volume collected from soil columns treated with sewage effluent was 450 mL. (The percolating rate of SE soil columns was too low and the process stopped before the end of leaching process.) Concentrations of Pb, Zn, Cu and Cd were determined in the obtained solutions.

Analytical methods

- Mechanical analyses of soil was performed according to the pipette method as described by Dewis and Feritas^[29]. Organic matter by oxidation with dichromate according to Walkley and Black^[29]. Total Carbonate Content (TCC) was determined gasometrically using Collins calcimeter and calculated as CaCO₃^[29]. Soil pH was measured in (1:1) soil: water suspension using single probe combination pH electrode (744 pH meter, Metrohm). Electrical Conductivity (EC) was measured in (1:1) soil: water extract using 3100 Conductivity Instrument. Cation Exchange Capacity (CEC) was determined using sodium acetate method, pH 8.2^[30].
- Total contents of Pb, Zn, Cu and Cd were extracted from the initial soil by aqua regia (HCl-HNO₃) according to the method described by Cottenie *et al.*^[31].

- Plant available Pb, Zn, Cu and Cd were extracted using 0.005 M DTPA (diethylenetriaminepentaacetic acid), 0.05 M CaCl₂ and 0.1 M TEA (triethanolamine), pH 7.3, as described by Lindsay and Norvell^[32].
- EDTA extractable Pb, Zn, Cu and Cd, were determined in nonpolluted soil using 0.01 M Na₂-EDTA, at soil solution ratio of 1:5
- Concentrations of Zn, Pb, Cu, Cd and Ca were measured using Flame Atomic Absorption Spectrophotometer (FAAS, Shimadzu, AA6200, Kyoto, Japan).
- Cl concentration in leaching solutions was determined using Ion Chromatography (761 compact IC, Metrohm). Dissolved organic carbon (DOC) of the leaching solutions was determined by titration using KMnO₄^[33]. Electrical conductivity (EC) was measured in leaching solution using 3100 Conductivity Instrument.

Statistical analysis: Data of Pb, Zn, Cu and Cd concentrations in all obtained leachates were statistically analyzed using SAS program^[34]. The results of ANOVA table showed insignificant differences between replicates.

RESULTS AND DISCUSSION

Chicken manure extract (CHCME), cow manure extract (COWME), Sewage effluent (SE), Na₂-EDTA and distilled water (H₂O) were used to examine the mobility of heavy metals in soil previously polluted with Pb, Zn, Cu and Cd. Both H₂O and EDTA are used for comparison. H₂O was used as a blank control due to its ability to remove, only, the readily soluble portion of the metal. Na₂EDTA solution might represent the worst-case situation of metal leaching in soils.

Lead: The results (Fig.1 a) show that, the first leachate of H₂O contains low Pb concentration of 3.3 mg L⁻¹, followed by sharp decrease, then gradual decrease reached zero after seventeen leachates. Concentrations of Pb in the first three leachates of COWME and SE (ranging from 8.7-1.9 and 6.0-1.5 mg L⁻¹, respectively) were much higher than those in H₂O. In the latter leachates, concentration decreased gradually to be close to that in H₂O. While, concentrations of Pb in the first three leachates of CHCME (ranging from 11.7-3.6 mg L⁻¹) were markedly higher than those reported for H₂O, COWME and SE. The latter leachates showed persistence at Pb concentration of about 2.5 mg L⁻¹, which proceeded to the end of leaching period. Contrary to the former leaching solutions, Pb concentrations in EDTA leachates were markedly high. The concentrations increased rapidly from 23.5, at first leachates, to 410 mg L⁻¹, after eight leachates, then decreased slowly to be about 250 mg L⁻¹, which proceed to the end of the leaching period. i.e.,

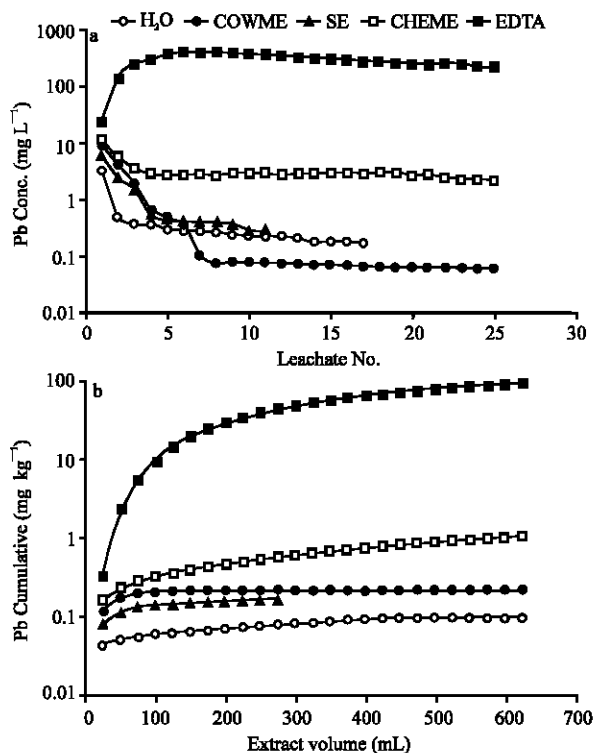


Fig. 1: Pb concentration (a) and cumulative (b) in leachates of cow and chicken manure extracts, sewage effluent, EDTA and H₂O, of polluted soil

EDTA has potential ability to mobilize additional amounts of Pb.

Except for EDTA, the leaching solutions used in this study (SE, COWME and CHCME) were able to mobilize only minimal portions (Fig. 1b) of soil Pb, 0.18, 0.24 and 1.1 mg kg⁻¹, respectively. These amounts are somewhat higher than that (0.1 mg kg⁻¹ soil) reported for H₂O. The total amounts of Pb removed in H₂O, SE, COWME and CHCME were found to represent only small percentages (0.05, 0.09, 0.12 and 0.55%, respectively) of total Pb previously added to soil. These results showed that, neither organic and inorganic ligands of COWME and SE, nor soluble Ca ions had potential ability to mobilize and/or displace considerable amounts of solid phase Pb. Also, the dissolved organic ligands of CHCME had slightly higher ability than SE- and COWME-ligands to form soluble complexes with soil Pb. These results indicated that, a very small portion of soil Pb resides in leachable form. A great portion of Pb might form inner sphere complexes with soil solid phase. Similar results were obtained by Chang *et al.*^[35]. They concluded that organic ligands in poultry litter extract might not be able to desorb Pb by forming soluble complexes. Also, they reported that

Pb had high affinity to soil solid phase. Zimdahl and Skogerboe^[36] demonstrated that soil had rather high capacities for immobilization of Pb. On the other hand, the total amount of Pb (97.8 mg kg⁻¹) mobilized in EDTA leachates of the present study was 90-500 times greater than that recorded for CHCME, COWME and SE extracts. The mobilized amount was found to represent 49% of the total Pb previously added to soil. Similar results, were recorded by Li and Shuman^[37]. They reported that EDTA leached nearly 25 and 40% of total Pb from polluted soil packed in columns. The high leaching of Pb with EDTA indicated that the formation of stable chelates was critical for the solubilization of Pb. More than 100 fold increases of lead concentrations in the biomass of crops were reported, when EDTA was applied to contaminated soils^[11]. Lead prefers to form chelate complexes with EDTA more than Zn and Cd do. The formation constant of Pb EDTA (log K=19) is higher than those for Zn (log K=17.5) and Cd (log K=17.4) by Norvell^[38]. These results imply that the mobility of soil Pb is uncertain under normal field processes including utilization of different sources of organic manure and sewage effluent.

Zinc: The results show that Zn concentration in the first leachates of all solutions is relatively high (ranging from 24.9-126 mg L⁻¹). Except for EDTA, Zn concentration in the latter leachates decreased slowly (Fig. 2a). The lowest Zn concentrations were recorded for H₂O. Except for the first leachate, SE and COWME contain, approximately, similar Zn concentrations (ranging from 25-1.0 mg L⁻¹). These concentrations are slightly higher than their counterparts in H₂O (ranging from 20-0.1 mg L⁻¹). Zn concentrations in CHCME leachates (ranging from 105-30 mg L⁻¹) were much higher than those recorded for H₂O, COWME and SE. Zn concentrations in CHCME leachates show persistency at relatively high concentration (about 30 mg L⁻¹), which proceed to the end of the leaching process. i.e., CHCME had potential ability to mobilize additional amounts of Zn as the leaching process continued. However, Zn concentrations in EDTA leachates increased from 126 to 354 mg L⁻¹. These concentrations are extremely higher than those recorded for all former leaching solutions. Moreover Zn concentration in EDTA leachates, proceed at high level of 262 mg L⁻¹ to the end of the leaching process. These results verify that EDTA had a potential ability to mobilize excessive amounts of soil Zn.

The total amount of Zn (Fig. 2b) removed in H₂O, which represents the readily soluble Zn, was relatively low (1.1 mg kg⁻¹). Both COWME and SE were able to mobilize amounts of Zn (1.4 and 2.1 mg kg⁻¹) slightly higher than that removed in H₂O. These results show that,

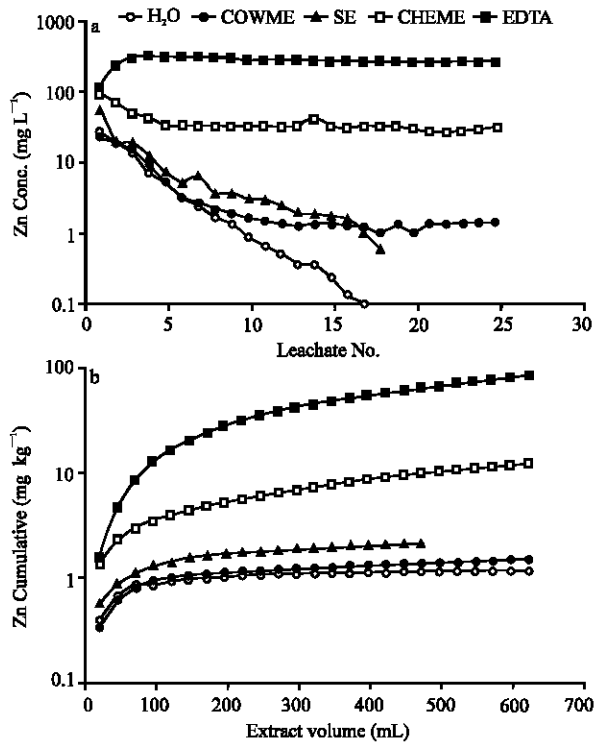


Fig. 2: Zn concentration (a) and cumulative (b) in leachates of cow and chicken manure extracts, sewage effluent, EDTA and H₂O, of polluted soil

the efficiency of both organic and inorganic ligands of COWME and SE, to mobilize soil Zn was too low. Also, soil Zn is not easily to be displaced by Ca cations of SE. i.e., soil Zn may be reside in non exchangeable form. It may be specifically adsorbed on soil solid phase. On the other hand, the amount of Zn mobilized in CHCME (12.9 mg kg⁻¹) was much higher than those reported for COWME and SE. i.e., The dissolved organic ligands of CHCME had higher efficiency than those of COWME, in forming soluble complexes with soil Zn. However, the total amounts of Zn mobilized in both COWME, SE and CHCME were found to represent only small percentages (0.36, 0.53 and 3.2%, respectively) of the total soil Zn. These results indicated that, Zn ion prefers association with soil solid phase rather than complexing with dissolved organic and inorganic ligands in solution. In other words, the bonds between Zn and soil solid phase are much stronger than those formed with solution dissolved ligands. Contrary to the four former leaching solutions, the results show the high efficiency of EDTA in mobilizing soil Zn. EDTA was able to mobilize high amounts (96.3 mg kg⁻¹) of soil Zn. This amount represents 24% of the total Zn previously added to soil. The

efficiency of EDTA could be attributed to solubilization of Zn by chelate formation^[38]. Similar results, were obtained by Li and Shuman^[37]. They reported that, leaching of Zn by EDTA solution was larger than that for poultry litter extract and CaCl₂, indicating a high potential to solublize soil Zn. In leachate volume of 400 mL, the total leaching of Zn in soil columns was about 34% of the total soil Zn. In general, these results, indicate the high affinity of Zn to soil solid phase. Based on these results, the threaten of Zn to environment, human health and contamination of ground water are uncertain under circumstances of Zn level matching that recorded for the present study.

Copper: The results showed three different trends for the change of Cu concentration in the leachates (Fig. 3a). Cu concentrations in the first leachate of both H₂O and SE were relatively low (1.4 and 1.2 mg L⁻¹, respectively), then decreased gradually to about 0.4 mg L⁻¹ which sustain to at the end of the leaching process. Also, Cu concentration in the first leachate of COWME was relatively low (1.2 mg L⁻¹) and close to that in H₂O and SE, followed by slightly decrease, then increased gradually to be 2.0 mg L⁻¹ before the end of the leaching process. A tendency for increasing Cu concentration was observed (Fig. 3 a and b) before the end of leaching process. This means that, as the time increases, Cu mobilized in COWME increases. Similar trends were observed for CHCME and EDTA. Although, Cu concentrations in the first leachate of both CHCME and EDTA (2.6 and 8 mg L⁻¹, respectively) were markedly higher than those reported for H₂O, SE and COWME, a sharp increases in Cu concentration reaching 111.8 and 98 mg L⁻¹, for CHCME and EDTA, respectively, were recorded for the latter leachates. These results verified that diffusion process is involved in the reaction of Cu with soil components. Barrow^[9] suggested that, the rapid surface sorption of Cu are followed by a subsequent slow transfer of the metals into soil fractions with tendency towards irreversibility, or at least a desorption rate that is significant slower than the adsorption rate. The results (Fig.3a) show that, Cu concentration of both CHCME and EDTA sustained stability at about 65 and 62 mg L⁻¹, respectively, to the end of the leaching process. Hence, these two leaching solutions had potential ability to mobilize further amounts of solid phase Cu.

The total amounts of Cu (Fig.3b) removed in H₂O, SE and COWME, were too small, 0.17, 0.15 and 0.37 mg kg⁻¹, respectively. These amounts represent small percentages (0.17, 0.15 and 0.37%) of the total Cu previously added to soil. i.e., both SE and COWME had low efficiency in mobilizing soil Cu. Except for readily soluble form, neither Ca²⁺ nor inorganic and organic ligands of SE and

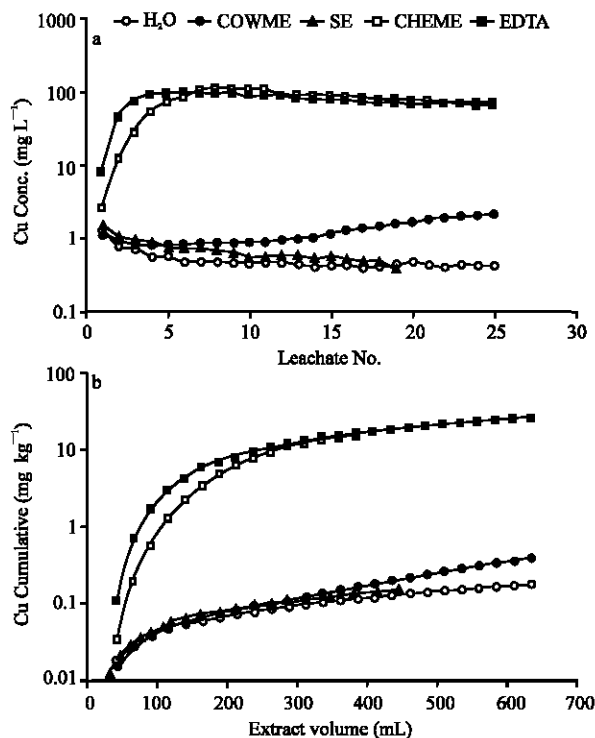


Fig. 3: Cu concentration (a) and cumulative (b) in leachates of cow and chicken manure extracts, sewage effluent, EDTA and H₂O, of polluted soil

COWME, are able to replace and/or form soluble complexes with soil Cu. The limited ability of both SE and COWME to mobilize soil Cu could be attributed to that, Cu ion is specifically adsorbed on the solid phase surface. An agreement with this conclusion could be derived from the statement of Alloway^[39] who reported that, in most agricultural soils at pH above 5.5, Cu is present as 'specifically' adsorbed ions and complexes. Thus specifically adsorbed Cu can't be removed by cation exchange when excessive amounts of Ca⁺² or other exchangeable ions are added to the soil. Based on these results, accumulation of Cu in the plants grown in polluted soil as well as contamination of ground water as a result of using sewage effluent and/or cow manure is uncertain. However, COWME had a potential ability to mobilize further amounts of Cu as the leaching process continued. (The latter part of the cumulative curve shows marked increase in Cu mobilized by COWME.) On the other hand, addition of chicken manure to Cu polluted soil should be avoided due to its high efficiency in mobilizing soil Cu. In the present study CHCME mobilized enormous amount (24.5 mg kg⁻¹) of soil Cu, which represents 24.5% of total Cu previously added to soil. The amount of Cu mobilized in CHCME was identical to that (24.5 mg kg⁻¹)

mobilized in EDTA solution (the chelating agent which typified as one of the strongest synthetic chelating agent), Stevenson^[28]. The dissolved organic ligands of CHCME prove high affinity to form soluble Cu-complexes, hence removing high quantities of soil Cu. In conclusion, Cu polluted soils need specific management with respect to organic manure utilization to avoid Cu phytotoxicity and ground water contamination as well.

Cadmium: The results (Fig. 4a) show that, the first leachates of all solutions contain high Cd concentrations. These concentrations varied widely among utilized leaching solutions, 49.5, 49.8, 203.2, 230.1 and 126 mg L⁻¹, for H₂O, COWME, SE, CHCME and EDTA, respectively. Except for EDTA, a sharp decrease in Cd concentration, followed by gradual decrease, was recorded for the latter leachates of all solutions. With respect to EDTA leachates, Cd concentrations show slow decrease and sustain at 10 mg L⁻¹ at the end of the leaching process. Increasing Cd concentration in the first leachates of all solutions, in particular of H₂O, verify that a relatively high portion of soil Cd resided in a readily soluble form.

The results (Fig. 4b) showed that, all utilized solutions succeeded in mobilizing varied amounts of soil Cd. The total mobilized amounts were, 1.54, 2.06, 4.83, 8.51 and 16.81 mg kg⁻¹ for H₂O, COWME, SE, CHCME and EDTA, respectively. These amounts were found to represent 7.7, 10.4, 24, 43 and 84% of the total amount of soil Cd. The immediate implication of these results is that a considerable amount of soil Cd (7.7 %) was found in a readily soluble form. SE was able to mobilize higher amounts of Cd than COWME. The higher efficiency of SE could be attributed to replacement of solution Ca ions for exchangeable Cd rather than formation of CdCl⁻ complex. Chemical composition of SE and COWME (Table 2) show that, Cl⁻ concentration in SE (7.65) was relatively lower than that of COWME (9.09 meq L⁻¹), whereas Ca concentration in SE (3.8) is four times that (0.99 meq L⁻¹) in COWME. However, the efficiency of CHCME in mobilizing Cd is rather high than those of former leaching solutions (SE and COWME). CHCME was able to mobilize 43% of total Cd content previously added to soil. The high efficiency of CHCME could be attributed to formation of soluble Cd complexes with organic ligands rather than inorganic ones and/or, replacement by Ca ions. These results verify that soil Cd is distributed among different chemical forms, water soluble, exchangeable and specifically adsorbed or inner-sphere complexed form. Li and Shuman^[38] reported that large portion of Cd previously added to soil existed in easily extractable form. Also, they reported that large portion of Cd resided in an exchangeable form, as the leaching of Cd

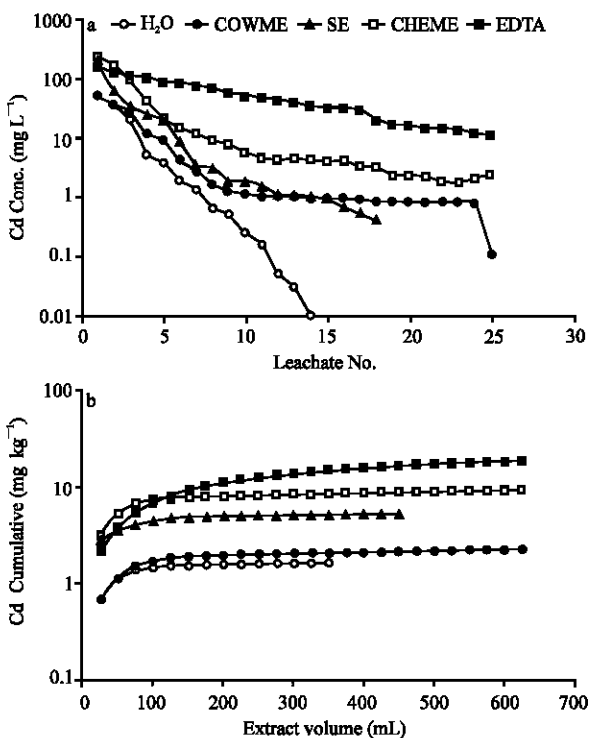


Fig. 4: Cd concentration (a) and cumulative (b) in leachates of cow and chicken manure extracts, sewage effluent, EDTA and H₂O, of polluted soil

with CaCl₂ was relatively high. The large portion of Cd existed in exchangeable fraction suggests that cation exchange and inorganic ligands such as Cl⁻ could effectively release soil Cd. Helal *et al.*^[40] reported that Cd adsorbed in alluvial and calcareous soils was partly irreversible. Sum of the amount of Cd desorbed in four successive extracts of 0.5 M CaCl₂ were found to represent 57 and 61% of those previously adsorbed by alluvial and calcareous soils, respectively. According to the hard-soft Lewis acid-base principles (HSAB), Cadmium is a soft Lewis acid and will therefore react and complex most readily with soft Lewis bases, such as chloride and hydroxyl groups^[41]. Competition with other metal ions, such as Ca, Co, Cu, Ni and Pb can inhibit the adsorption of Cd. Christensen^[42] found that, increasing soluble Ca concentration from 0.001 to 0.01 M, reduced Cd adsorption capacity of sandy loam by 67%.

Among all leaching solutions, EDTA had the highest efficiency in mobilizing soil Cd. It was able to mobilize 16.81 mg Cd kg⁻¹ soil. This amount was found to represent 84% of total Cd previously added to soil. The highest efficiency obtained for EDTA in the present study, was in agreement with the results of Li and Shuman^[37]. They reported that, the leaching of Cd with

Table 3: The total amounts of heavy metals (mg kg⁻¹) mobilized in extract solutions

Leaching solution	Heavy metal			
	Pb	Zn	Cu	Cd
H ₂ O	0.10	1.10	0.17	1.54
SE	0.18	2.10	0.15	4.80
COWME	0.23	1.44	0.37	2.06
CHCME	1.10	12.90	24.50	8.50
EDTA	97.80	96.30	24.40	16.81

EDTA in the metal-amended soil was greater than that with, either poultry litter extract or CaCl₂. It is inferred from the increasing of mobilized amounts of Cd that there is low affinity between Cd ion and soil solid phase. Complexation of Cd with certain organic ligands in the soil solution may have major effects on the adsorbed amounts. Farrar and Pickering^[43] found that EDTA prevented the adsorption of Cd over the pH range 3-11. In this connection, the behavior of Cd is rather different from that of Pb and Zn, which have high affinity to soil solid phase. Cadmium was identified as being the most mobile element, having the highest extractability, followed by Zn and Cu. Lead was shown to be poorly mobile or nonmobile^[44]. Alloway^[39] reported that Cd tends to be more mobile in soils and, therefore, more available to plants than many other heavy metals, including Pb and Zn. It was shown that the selectivity of several soil adsorbents for Cd was lower than that for Pb and Zn. Based on these results, application of chicken manure, cow manure and/or sewage effluent, to Cd polluted soil may lead to a considerable increase in mobilization of Cd. Also, furrow irrigation, may contribute to Cd release in polluted soil, since the results obtained in this work have show that distilled water was able to mobilize considerable amounts (7.7%) of the total Cd added to soil. Thereby, accumulation of Cd in plants grown in polluted soils as well as contamination of ground water, are more likely to occur. Focus on the total amounts of Pb, Zn, Cu and Cd, (Table 3) mobilized in the leaching solutions shows that;

1. Among the tested heavy metals, considerable amounts of Cd and to a lesser degree Zn, are found in both readily soluble and exchangeable form as extracted by H₂O (1.54 and 1.1 mg kg⁻¹) and SE (4.8 and 2.1 mg kg⁻¹ for Cd and Zn, respectively),
2. Except for Pb (1.1 mg kg⁻¹), CHCME had high efficiency in mobilizing soil-metals; particularly Cu (24.5) and to a lesser degree Zn (12.9) and Cd (8.5 mg kg⁻¹). Efficiency of CHCME to mobilize Cu was identical to that of EDTA (24.5 mg kg⁻¹), the strongest chelating agent;

3. Among tested metals, Pb had the highest affinity for soil solid phase. Only, minimal portions of soil Pb (less than 0.55%) were mobilized in H₂O, SE, COWME and CHCME and
4. EDTA solution had high potential to extract excessive amounts of both Pb, Zn and Cu, as the leaching process continued, since the last 5 leachates of EDTA (Fig.1a, 2a and 3a) contain invariable high concentrations of Pb (250), Zn (365) and Cu (66 mg L⁻¹).

The mobility of the tested heavy metals varied widely among utilized leaching solutions. While soil Cd proved high mobility in both chicken and cow manure extracts and sewage effluents, Pb had high affinity to soil solid phase. All utilized solutions were able only to mobilize minimal amounts of soil Pb. On the other hand, soil Cu proves high mobility, only, in chicken manure extract, but at the same time it was almost immobile in cow manure extract and sewage effluent. Soil Zn proved low mobility in chicken manure extract, but it was nearly immobile in both cow manure extract and sewage effluent.

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