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Mobility and Distribution of Zinc, Cadmium and Lead in Calcareous Soils Receiving Spiked Sewage Sludge

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Leaching column experiments were conducted to determine the degree of mobility and the distribution of zinc (Zn), cadmium (Cd), and lead (Pb) because of an application of spiked sewage sludge in calcareous soils. A total of 20 leaching columns were set up for four calcareous soils. Each column was leached with one of these inflows: sewage sludge (only for two soils), spiked sewage sludge, or artificial well water (control). The columns were irrigated with spiked sewage sludge containing 8.5 mg Zn l^{-1}, 8.5 mg Cd l^{-1}, and 170 mg Pb l^{-1} and then allowed to equilibrate for 30 days. At the end of leaching experiments, soil samples from each column were divided into 18 layers, each being 1 cm down to 6 cm and 2 cm below that, and analyzed for total and extractable Zn, Cd and Pb. The fractionation of the heavy metals in the top three layers of the surface soil samples was investigated by the sequential extraction method. Spiked sewage sludge had little effect on metal mobility. In all soils, the surface soil layers (0-1 cm) of the columns receiving spiked sewage sludge had significantly higher concentrations of total Zn, Cd and Pb than control soils. Concentration of the heavy metals declined significantly with depth. The mobility of Zn was usually greater than Cd and Pb. The proportion of exchangeable heavy metals in soils receiving spiked sewage sludge was significantly higher than that found in the control columns. Sequential extraction results showed that in native soils the major proportion of Zn and Pb was associated with residual (RES) and organic matter (OM) fractions and major proportion of Cd was associated with carbonate (CARB) fraction, whereas after leaching with spiked sewage sludge, the major proportion of Zn and Pb was associated with Fe-oxide (FEO), RES, and CARB fractions and major proportion of Cd was associated with CARB, RES and exchangeable (EXCH) fractions. Based on relative percent, Cd in the EXCH fraction was higher than Zn and Pb in soils leached with spiked sewage sludge.

Keywords Calcareous soil, heavy metal, metal mobility, selective extraction, spiked sewage sludge

Introduction

There is a concern that increased anthropogenic inputs of heavy metals in soils may result in transport of these metals in soil profile, leading to the increased concentrations of heavy metals in the ground or surface waters (Hooda and Alloway, 1993). The application of sewage sludge on agricultural land is a common practice around the world, including Iran. Soil contamination with anthropogenic heavy metals resulting from application of sewage

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sludge, fertilizer, and industrial activities is widespread. Heavy metals are usually persistent in soil, with residence times in the order of millennia (McGrath, 1987).

Land application of sewage sludge has been shown to benefit crop production and improve soil quality (Basta, 1995, 2000), because this process provides organic materials and offers the possibility of recycling plant nutrients. However, high loadings of metals in soil may increase plant uptake and therefore enter the human food supply. Lead (Pb), copper (Cu) and nickel (Ni) are potentially toxic to plants and animals and have been shown to accumulate in the food chain (Logan and Chaney, 1983). Zinc (Zn) is an essential micronutrient for plants, but at high concentrations it is phytotoxic and may reduce the productivity of the land. Cadmium (Cd) is highly toxic to plants, animals, and humans. Zinc is relatively mobile in soils (Li and Shuman, 1996). Although Cd generally is present in much smaller concentrations than Zn, it also considered to be mobile (Alloway and Jackson, 1991). Riise *et al.* (1994) found that the amount of anthropogenic Cd entering the mobile fraction is of great importance, as this fraction is believed to be more bioavailable. Zinc and Cd have similar chemical properties and behavior in soils (Bergkvist, 1986), but Pb is much less mobile (Camobreco *et al.*, 1996). Although Pb also can form complexes with organic acids, it is strongly bound to the soil matrix, and soluble Pb complexes will not greatly impact its solubility (He, 1997).

Benefits from sewage sludge application on croplands, therefore, should be evaluated with consideration of the potential heavy metal hazards. The sewage sludge may contain heavy metals that, when applied to soil, are rapidly retained as insoluble compounds and adsorbed to soil surface (Berti and Jacobs, 1998). However, downward movement of heavy metals in sandy soils with low cation exchange capacity, due to the land application of sewage sludge, may occur (Gove *et al.*, 2001). Retention of heavy metals in soils and their accumulation in plant tissues have caused concerns about their extensive use on cropland.

The movement of heavy metals in soil is greatly affected by the physicochemical forms in soil solid phase (Li and Shuman, 1996) and adsorption (Berti and Jacobs, 1998). Evidence of metal movement indicates that metals can move under conditions where large amounts of water have been applied (Lund *et al.*, 1976), or after long-term additions of residues (Schirado *et al.*, 1986; Siebe, 1995). Furthermore, sewage sludge tends to increase soil acidity as a result of diprotonation of organic matter decomposition and mineralization of NH_4^+-N. Increased soil acidity could cause greater solubility of metals and consequently enhanced their plant availability and leaching potential, particularly in soils with poor buffering capacity (Hooda and Alloway, 1993). The mobility of heavy metals depends not only on the total concentration in soil but also on soil properties, metal properties, and environmental factors (He *et al.*, 2004).

Total heavy metal contents provide little information on the mobility and bioavailability of the heavy metals. Heavy metals in soil are considered to be distributed among several phases which include water soluble phase, exchangeable phase, organic associated phase, carbonate associated phase, bound and occluded in oxides and secondary clay minerals phase and residual within the primary mineral lattice phase (Li and Shuman, 1996). Water soluble and exchangeable fractions are considered readily mobile and bioavailable, whereas other metal fractions, especially a residual fraction, are considered immobile and tightly bound and may not be expected to be released under natural conditions. Sequential extraction is widely used to estimate the amounts and proportions of metals in soil and to predict bioavailability and metal leaching.

Use of sewage sludge has become inevitable for irrigation to compensate rapidly increasing water demands in many arid and semiarid regions. In some part of the arid and semi-arid regions in Iran, such as Hamadan plains in the state of Hamadan, sewage sludge constitutes important source of supplemental irrigation due to inadequate availability of fresh surface and groundwater. The irrigated area with sewage sludge has been growing as sewage sludge volume increases.

The enrichment or spiking of sewage sludge with heavy metals for experimental purposes is a widely used technique to increase the rate of build up of metals in soils treated with sludge without having to apply excessive amounts of sewage sludge to the soil. Little information is available about the extent of mobility and distribution of Zn, Cd and Pb due to application of spiked sewage sludge in calcareous soils. Therefore, the distribution and changes in different chemical pools of Zn, Cd and Pb in calcareous soils receiving spiked sewage sludge were examined by soil column leaching experiments.

Materials and Methods

Soil Samples

Four surface soils (0–30 cm) were collected from fields currently cultivated with wheat in the Hamadan area, western Iran. The climate of the region is semiarid with a mean annual precipitation of 300 mm and mean annual temperature is 10 °C. Soil samples were air dried, sieved (2 mm), and stored. Soil properties (Table 1) were determined according to methods given in Rowell (1994). The four soils are varied in their chemical and physical properties (Table 1), but represent the study area. The soils had similar pH and EC but differed substantially in texture, calcium carbonate content and cation exchange capacity. The soils from Kabotar ahang and Dehpiaz contained significant amounts of $CaCO_3$, whereas the other two soils had little $CaCO_3$. The Kabotar ahang soil was more clayey than the other soils and possessed a correspondingly greater CEC. These soils had low concentrations of Zn, Pb and Cd, (except the Kabotar ahang).

Table 1
Selected physical and chemical properties

Properties Soil No.	Bahar 1	Azandarin 2	Dehpiaz 3	Kabodar ahang 4
Classification	Typic Calcixerepts	Typic Calcixerepts	Typic Xerofluvents	Typic Xerocrepts
Clay (g kg^{-1})	135	157	254	431
Silt (g kg^{-1})	93	223	216	357
Sand (g kg^{-1})	772	620	530	212
pH	7.2	7.1	7.5	7.7
EC (dS m^{-1})	0.8	0.5	0.9	1.1
CEC (cmol$_c$ kg^{-1})	15.0	12.6	11.8	16.8
OM (g kg^{-1})	3	37	21	13
$CaCO_3$ (g kg^{-1})	58	47	100	200
Total Zn (mg kg^{-1})	50.2	56.2	57.7	72.1
Total Cd (mg kg^{-1})	1.4	1.3	1.5	3.2
Total Pb (mg kg^{-1})	52.0	57.0	46.0	70.0

Leaching Experiments

Glass tubes, 4.8 cm diameter and 40 cm long were packed uniformly with air-dried soil, resulting in a 30 cm soil core. The soil cores had bulk density ranges of 1.3–1.4 g cm^{-3}. A complete randomized block design with two replications was used and a total of 20 leaching columns were set up for four soils. Each column was then leached with one of these inflows: sewage sludge (only for two soils), spiked sewage sludge, or artificial well water. The sewage sludge was spiked with 8.5 mg Zn l^{-1},8.5 mg Cd l^{-1}, and 170 mg Pb l^{-1}. A quantity of 5.5 litre freshly prepared spiked sewage sludge was applied to each column for 30 days. Thus the amount of Zn, Cd and Pb was 47 and 935 mg per column, respectively. To make a comparison with the irrigation water typical of the study area, a leaching column with artificial well (control) water was used in four soils. In the studied area calcium is the dominate ion in water wells and concentrations of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} are on average, 147, 72, 43 and 2 mg l^{-1} respectively (Jalali, 2002). Thus leaching of heavy metals with artificial well water simulate the effects of irrigation water in the area.

Sequential Extractions of Heavy Metals in Leached and Native soils

At the conclusion of the leaching experiments, the soil columns were allowed to freely drain, and split open. The soil samples from each column were divided into 1 cm thick for the top 6 layers and 2 cm thick for the next 12 layers. Samples from each layer were analyzed for extractable Zn, Cd and Pb content (0.005 mol of DTPA pH: 7.2 1:10 w/v ratio) and total (digested by 4 M HNO_3 for 12 h). Among numerous sequential extraction methods, the method proposed by Tessier *et al.* (1979) is most widely used method, especially for calcareous soils. Soil samples from first three layers (0–1, 1–2, and 2–3 cm) were sequentially extracted using Tessier *et al.* (1979). In this method six fractions that heavy metals bound were (1) exchangeable (EXCH), (2) organic matter (OM), (3) carbonate (CARB), (4) bound and occluded in Mn oxides (MNO), (5) bound and occluded in Fe oxides (FEO) and (6) residual (RES). Two grams of each soil sample were weighed into a 50 ml centrifuge tube and different fractions were extracted by the sequential fractionation procedure: EXCH, soil extracted with 20 ml 1 M NH_4OAc (pH = 7) for 30 minutes at room temperature with continuous agitation, CARB, residue from the EXCH fraction extracted with 20 ml 1 M NaOAc (pH = 5) for 5 hours with continuos agitation, MNO, residue from CARB fraction extracted with 20 ml 0.1 M NH_2OH. HCl in 0.1 M HNO_3 for 30 minutes with continuos agitation, FEO, residue from Mn oxides fraction extracted with 20 ml 0.04 M NH_2OH. HCl in 25% (v/v) acid acetic for 6 hours in a water bath (96°C) and at an occasional agitation, OM, residue from FEO fraction extracted with 5 ml 0.1 M HNO_3 and 10 ml 30% H_2O_2 for 5 hours in a water bath (85°C) and an occasional agitation. After cooling, 15 ml 3.2 M NH_4OA_C in 20% HNO_3 is added and shaken for 30 minutes. The RES was calculated from the difference between the concentration of total metal and the sum of the first five fractions. After each sequential extraction, supernatant was first separated by centrifugation and a aliquot was analysed for Zn, Cd and Pb.

All statistical analysis was performed using an SAS package (SAS Institute Inc.).

Results and Discussion

The Zn, Cd and Pb Concentrations in the Leachate

The Zn, Cd and Pb concentrations of leachate samples collected from these soil columns were all below the detection the limits (0.01 mg l^{-1}) as measured by the flame atomic

Table 2
Effects of spiked sewage sludge on total heavy metal concentrations (mg kg^{-1}) in soil layers

Heavy metal	Soil layers	Soil 1	Soil 2	Soil 3	Soil 4
Zn	0–1 cm	83.9	90.3	87.0	116.0
	1–2 cm	62.6	80.0	66.5	79.4
	2–3 cm	53.2	57.5	57.5	74.8
	3–4 cm	51.2	56.1	55.0	68.2
	4–5 cm	50.0	54.0	54.1	69.8
	5–10 cm	49.2	52.0	54.0	69.1
	>10 cm	47.0	52.0	54.0	69.0
Cd	0–1 cm	53.6	47.1	53.1	52.1
	1–2 cm	2.5	12.5	4.4	9.1
	2–3 cm	1.6	3.0	2.5	3.7
	3–4 cm	1.4	1.6	1.5	3.0
	4–5 cm	1.3	1.4	1.3	3.1
	5–10 cm	1.3	1.3	1.3	3.0
	>10 cm	1.2	1.2	1.3	3.0
Pb	0–1 cm	814.5	780.0	900.0	975.0
	1–2 cm	132.0	279.0	84.0	138.7
	2–3 cm	55.5	82.5	65.6	63.7
	3–4 cm	51.5	70.0	50.0	60.0
	4–5 cm	50.0	58.0	49.0	72.0
	5–10 cm	50.0	58.0	46.0	72.0
	>10 cm	50.0	57.0	46.0	70.0

adsorption spectrophotometry and were below World Health Organization drinking water quality guidance limits, suggesting that sewage sludge application is unlikely to present a problem for water quality if the results of this study are representative of field losses.

Retention and Distribution of Total Zn, Cd and Pb in Soil Profile

A significantly greater concentration of total Zn, Cd and Pb was found in all soils receiving spiked sewage sludge (Table 2). Most of the added heavy metals accumulated in the 0–1 cm soil layer. In all columns receiving spiked sewage sludge, the heavy metal concentration decreased significantly with soil layers. The drop in Zn, Cd and Pb content down the soil column was more pronounced in Kabodar ahang soil, than that for the other soils. The Zn concentration in the second layer (1–2 cm) leached with spiked sewage sludge was less than of that recorded for the first layer (Table 2). The Cd concentration of soil samples collected in the first layer (0–1 cm) was approximately eleven times (average of four soils) greater than of that of second layer. The Pb concentration of soil samples collected in the first layer (0–1 cm) was approximately seven times more than of that recorded in the second layer.

In general the results indicate that anthropogenic heavy metals were largely retained and accumulated in the surface layer of soils.

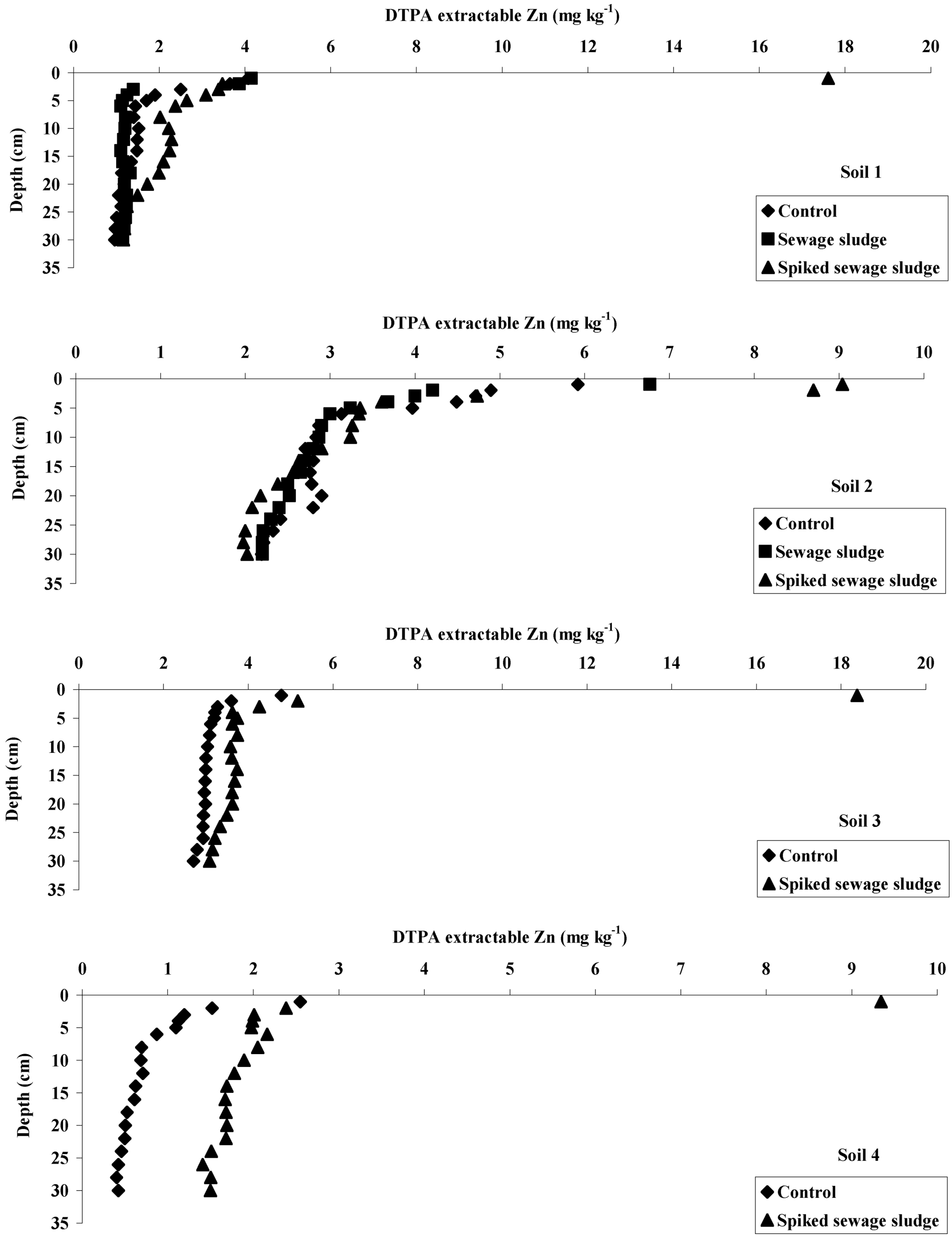

Figure 1. Vertical distribution of DTPA-extractable Zn concentration in spiked sewage sludge treated soil columns at the end of leaching experiment.

Vertical Distribution of DTPA-Extractable Heavy Metals in Soil Columns

The concentration of total heavy metals may not explain the degree of adsorption. The distribution of DTPA-extractable metals across the various depths is shown in Figures 1–3. In the spiked sewage sludge the extractable heavy metals were mostly concentrated in the

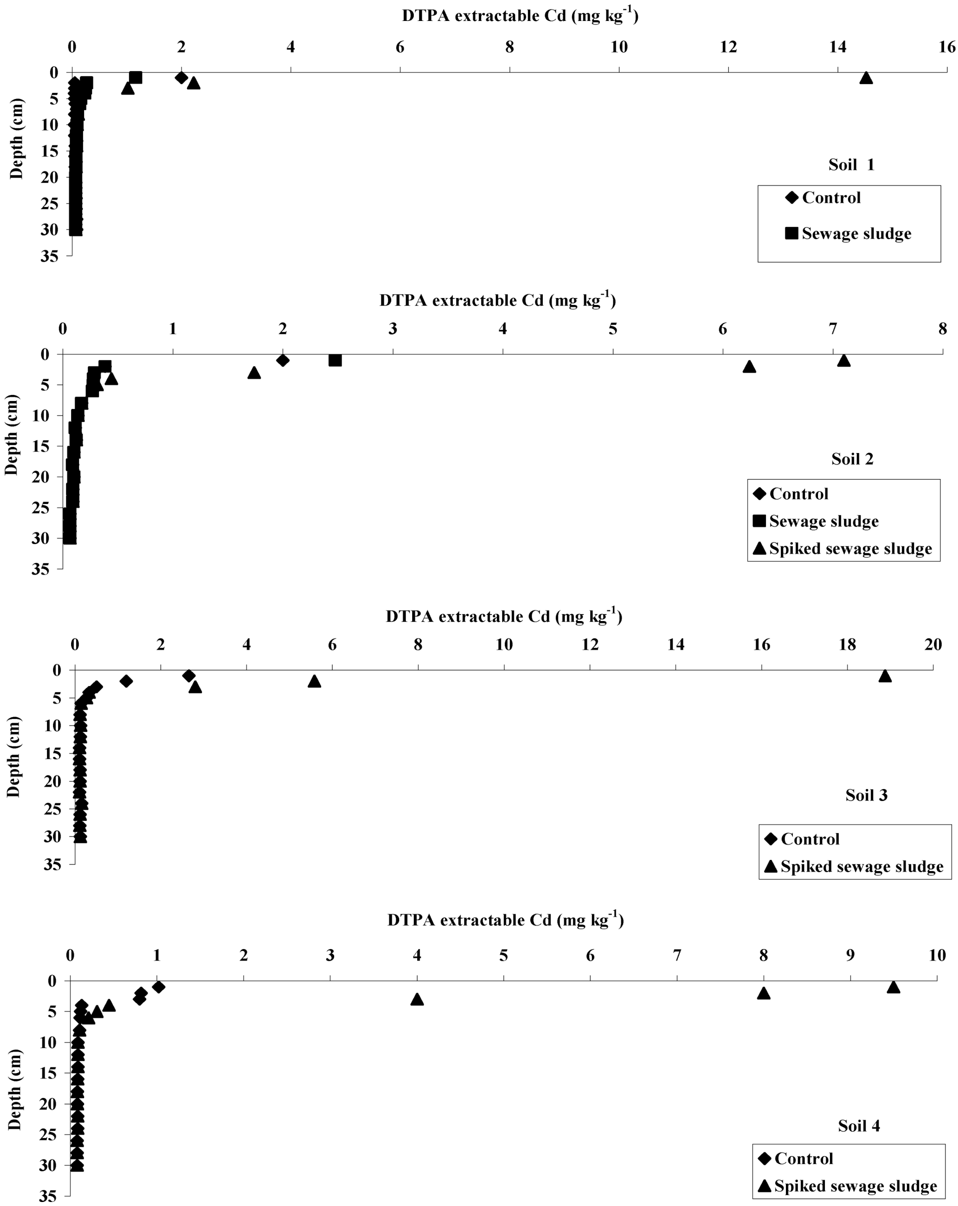

Figure 2. Vertical distribution of DTPA-extractable Cd concentration in spiked sewage sludge treated soil columns at the end of leaching experiment.

0–15 cm soil layers and declined significantly in the 15–30 cm. The amount of extractable metals in the control columns were substantially smaller than (24.0%) the total metal.

Cadmium mostly accumulated in the 0–1 cm soil layer and there was significant difference among treatments in Cd concentration in the 0–8 cm depth. Cadmium concentrations decreased dramatically in the 8–30 cm layer. Zinc followed a similar pattern of high accumulation as those of Cd in the 0–1 soil layer and low in the next layers in all treatments. Lead mostly accumulated in the 0–1 cm soil layer and there was significant difference

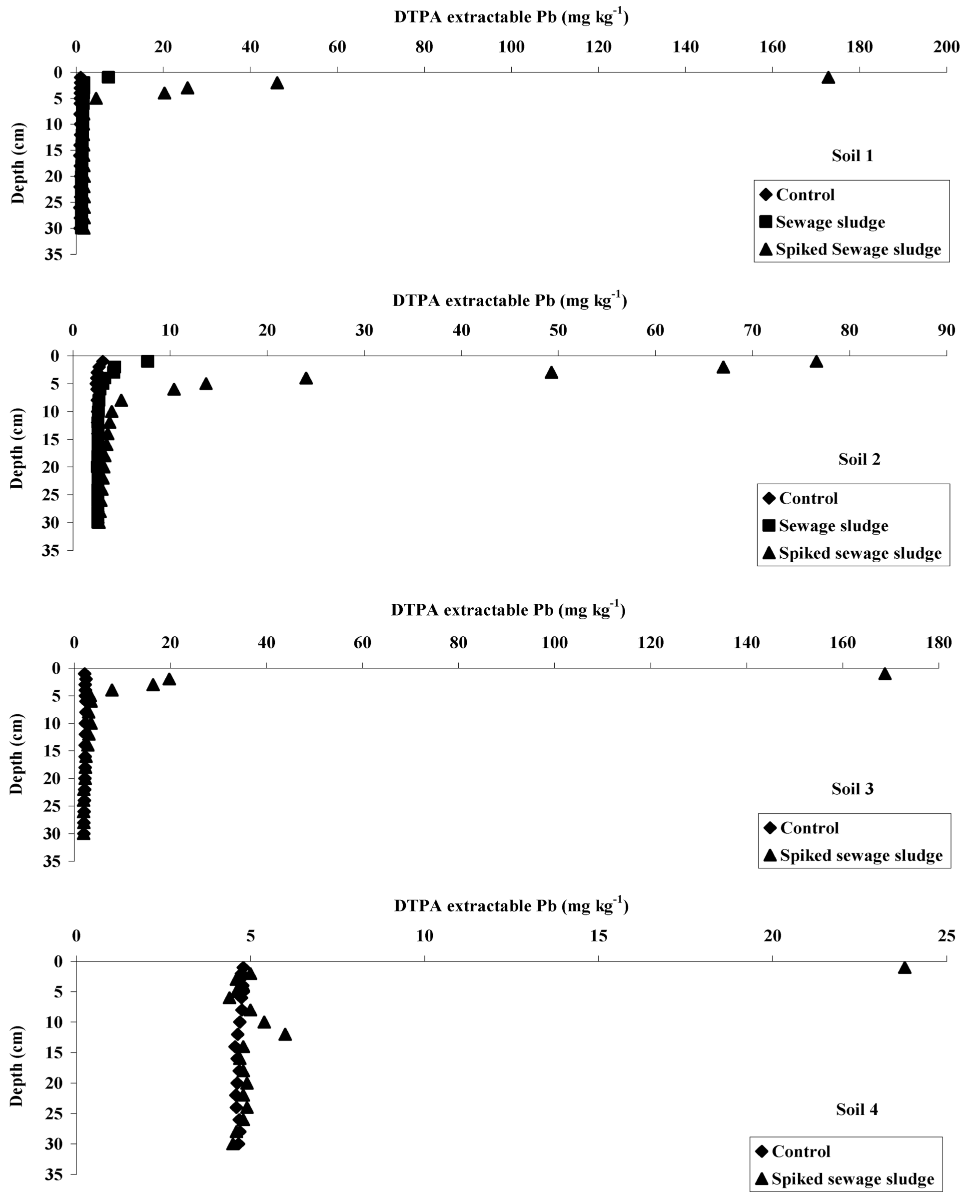

Figure 3. Vertical distribution of DTPA-extractable Pb concentration in spiked sewage sludge treated soil columns at the end of leaching experiment.

among treatments in Pb concentration in the 0–5 cm depth. Lead concentrations decreased dramatically in the 5–30 cm layer.

The results indicates that most of the Zn, Cd and Pb retained by the surface layers were labile and capable of resolubilization and migration which with further wastewater applications. Brown and Thomes (1983) applied secondary-treated sewage sludge effluent, adjusted to contain slightly less than 1 mg l^{-1} each of Cd, Cu, Ni, Pb and Zn to undisturbed soils varying in texture. The effluent was applied weekly for a period of one year and the leachate water and soil samples were collected periodically to evaluate the mobility of the metals. They found that after one year of effluent application, increases in metal concentrations were greatest at the surface and decreased rapidly with depth down the soil profile, with no significant increases reported below 25 cm depth.

Hinz and Selim (1994) discussed the processes of heavy metal interaction with soils including adsorption on clay and organic matter with very high-binding energies, and Zn precipitation on oxides, hydroxides and carbonates. The downward movement of metals was greatest in Bahar soil, which is consistent with the soils lower organic and clay contents. The presence of $CaCO_3$, appears to cause heavy metal precipitation because of the elevated pH cause metal hydrolysis these soils. However, it is difficult to quantify the relative importance of different interaction because of the complex and chemical heterogeneity of soils (Hinz and Selim, 1994).

Changes in Sequential Fractions of Zn, Cd and Pb After Leaching

Tables 3, 4, and 5 show Zn, Cd, and Pb partitioning among the six fractions, before and after leaching. Before leaching, the distribution pattern among the six fractions differed between the heavy metals and also among the soils. Portions of the three heavy metals added to the soils appeared in each fraction (Tables 3-5). Native soils had a higher concentration of Zn and Pb in RES, OM and FEO fractions (Tables 3 and 4). A higher concentration of Cd was found in CARB and MNO fractions in native soils (Table 5). The EXCH fraction of Zn, Cd and Pb represented 0.66–1.6, 6.06–21.5 and 0.9–4.6% of the total, respectively. The CARB fraction of Zn, Cd and Pb represented 3.1–6.8, 40–57.2 and 7.7–25.3%, respectively, and there was not an apparent relationship between CARB fraction and soil $CaCO_3$ content. The OM fraction involving Pb accounted for higher percentages of the total (16.2–27.7%) than Cd (1.1–9.5%), reflecting the strong binding of Pb with OM. The proportion of RES fraction of these metals was also variable, ranging from 45.9–65.5% for Zn, 0.25–6.4% for Cd, and 25.3–49.2% for Pb. Thus, the dominant fraction of Zn and Pb in the native soils was RES fraction, with very low amounts in the EXCH fraction. In general the distribution pattern was almost similar between Zn and Pb, suggesting that the background metals were mainly immobilized within the crystalline and secondary minerals and these metals are essentially non-labile.

After leaching, the chemical fractionation of Zn, Cd and Pb in soils receiving artificial well water were not significantly different from that of the native (Tables 3–5), indicating this irrigation water had little effect on metal distribution in these soils. After leaching, the chemical fractionation profiles of Zn, Cd and Pb in soils receiving spiked sewage sludge were significantly different from that of the control (Tables 3–5). When spiked sewage sludge was added to these soils, the concentration of Zn, Cd and Pb bound to the OM fraction decreased, with a parallel increase in other fractions, especially the RES fraction (Tables 3–5). The CARB, RES, MNO and FEO fractions of Zn, Cd and Pb also had more contributions to total metals retained in the sewage sludge spiked soils than that of the control.

The distribution pattern among the six fractions differed between Zn, Cd and Pb and between the soils leached with sewage sludge or spiked sewage sludge. Between 9.8 to 31.5% of the total Zn, in spiked sewage sludge soils, was associated with the CARB fraction and between 28.5 to 50.6% were in the RES fraction in the 0–1 cm soil layer (Figure 4). The Zn-RES fraction in soils leached with spiked sewage sludge increased in layers 2 (1–2 cm) and 3 (2–3).

Table 3
Zinc in the soil fractions in different treatments

Treatment	Depth (cm)	EXCH	CARB	MNO	FEO	OM	RES
		Soil fractions (mg kg^{-1})					
Soil 1							
Spiked sewage sludge	0–1	3.29a	26.46a	10.71a	5.18a	9.01a	29.31a
	1–2	2.77a	2.42b	3.21b	4.42b	8.32b	41.44b
	2–3	0.87b	1.64c	1.54c	3.99c	5.97c	39.19b
Sewage sludge	0–1	0.5a	2.33a	2.94a	5.48a	9.07a	32.06a
	1–2	0.46b	1.95b	1.79b	4.06b	8.79b	32.95b
	2–3	0.44b	1.62c	1.56c	3.47b	6.12c	35.78b
Control	0–1	0.45	2.12	2.11	3.75	8.94	32.22
Native	—	0.46	1.57	2.15	3.74	9.37	32.9
Soil 2							
Spiked sewage sludge	0–1	1.55a	24.95a	6.46a	21.27a	10.29a	25.75a
	1–2	0.92b	3.02b	3.04b	4.47b	7.85b	40.72b
	2–3	0.88b	2.06c	1.24b	3.33b	3.99c	46.003b
Sewage sludge	0–1	0.76a	2.48a	6.93a	8.92a	6.61a	31.29a
	1–2	0.29b	2.39b	2.57b	6.67a	4.66a	36.42a
	2–3	0.12b	1.98c	2.04b	5.02a	4.36a	34.98a
Control	0–1	0.38	2.55	6.07	5.85	10.23	31.72
Native	—	0.37	2.04	6.08	5.86	11.91	29.91
Soil 3							
Spiked sewage sludge	0–1	2.58a	10.82a	7.58a	23.65a	11.73a	30.64a
	1–2	0.69b	3.31b	2.83b	6.93b	8.25b	44.49a
	2–3	0.36c	2.98b	2.51b	6.39b	7.38c	37.89a
Control	0–1	0.38	2.65	2.54	9.45	17.35	25.26
Native	—	0.39	2.13	2.47	7.72	18.36	26.59
Soil 4							
Spiked sewage sludge	0–1	2.34a	11.33a	1.73a	35.37a	6.52a	58.73a
	1–2	0.081b	1.08b	0.61b	6.13b	3.36b	68.14b
	2–3	0.004b	0.95b	0.46b	4.17b	3.01b	66.19b
Control	0–1	1.16	5.15	1.55	12.44	11.31	38.81
Native	—	1.19	4.87	1.02	9.97	12.36	42.72

Values within a column followed with the same letter are not significantly different at the 0.05 probability level.

In general, for soils receiving spiked sewage sludge, the largest portion of Zn was found in RES fraction (average of three layers). Thus in this treatment, the added Zn was mainly partitioned into the RES, FEO and OM fractions and the Zn in each fraction generally in the order RES > FEO > OM > CARB > MNO > EXCH. In soil leached with sewage sludge Zn followed the sequence: RES > OM > FEO > MNO > CARB > EXCH. The proportion of Zn in the RES fraction in all three layers was more than the other fractions in soil leached with sewage sludge. These results were similar to the results observed by

Table 4
Cadmium in the soil fractions in different treatments

Treatment	Depth (cm)	Soil fractions EXCH (mg kg^{-1})	CARB	MNO	FEO	OM	RES
Soil 1							
Spiked sewage sludge	0–1	10.51a	22.4a	5.61a	1.52a	0.75a	12.83a
	1–2	0.58b	1.22b	0.32b	0.23b	0.135b	0.01b
	2–3	0.21b	0.91c	0.12c	0.12b	0.13b	0.16b
Sewage sludge	0–1	0.23a	0.84a	0.34a	0.10a	0.10a	0.007a
	1–2	0.21a	0.61a	0.19b	0.10a	0.10a	0.37b
	2–3	0.19a	0.52a	0.15c	0.10a	0.10a	0.49b
Control	0–1	0.21	0.84	0.12	0.11	0.12	0.02
Native	—	0.19	0.81	0.11	0.10	0.135	0.09
Soil 2							
Spiked sewage sludge	0–1	5.57a	5.4a	3.17a	2.91a	0.61a	29.45a
	1–2	1.83b	5.14a	1.11b	0.57b	0.31b	3.57b
	2–3	0.54c	1.83a	0.23c	0.21b	0.15c	0.12b
Sewage sludge	0–1	0.77a	1.91a	0.51a	0.13a	0.31a	0.009a
	1–2	0.10b	1.27b	0.32b	0.10a	0.10b	0.04b
	2–3	<0.10b	0.99c	0.10c	<0.10b	0.10b	0.03b
Control	0–1	0.13	0.91	0.71	0.27	0.23	0.05
Native	—	0.28	0.52	0.35	0.10	<0.10	0.045
Soil 3							
Spiked sewage sludge	0–1	2.09a	12.48a	6.61a	2.26a	0.51a	29.15a
	1–2	0.39a	1.51b	0.56b	0.17a	0.18b	1.76b
	2–3	0.29a	0.85b	0.37b	0.08a	0.13c	0.83b
Control	0–1	0.12	1.01	0.35	0.084	0.098	0.09
Native	—	0.10	0.84	0.33	0.13	0.11	0.05
Soil 4							
Spiked sewage sludge	0–1	7.77a	23.24a	6.76a	7.01a	0.27a	7.07a
	1–2	0.75a	3.41b	1.21b	0.91b	0.15b	0.41b
	2–3	0.18c	2.09b	0.74b	0.49b	0.09c	0.08c
Control	0–1	0.51	1.12	0.91	0.62	0.13	0.08
Native	—	0.37	1.32	0.74	0.57	0.15	0.008

Values within a column followed with the same letter are not significantly different at the 0.05 probability level.

Obrador *et al.* (2003). They found that about 92% of Zn in a calcareous soil was in residual fraction.

Between 11.5 to 44.6% of the total Cd, in spiked sewage sludge soils, was associated with the CARB fraction and 13.6–62.5% resided in the RES fraction in the 0–1 cm soil layer (Figure 5). On average 29 and 2.2% of the Cd was associated with the CARB and OM fractions, with the CARB fraction having the greatest. Cadmium in CARB fraction was increased in both soils treatments in the next two layers. The results indicate that after

Table 5
Lead in the soil fractions in different treatments

Treatment	Depth (cm)	EXCH	CARB	MNO	FEO	OM	RES
		Soil fractions (mg kg^{-1})					
Soil 1							
Spiked sewage sludge	0–1	40.21a	460.95a	31.21a	56.55a	57.11a	168.48a
	1–2	3.12b	29.05b	9.63b	13.75b	26.44b	50.01b
	2–3	1.51b	18.32b	7.32b	7.02b	13.72c	6.11c
Sewage sludge	0–1	1.31a	18.15a	11.02a	6.64a	12.81a	10.57a
	1–2	0.83b	15.39a	9.62b	6.07b	11.48b	12.61a
	2–3	0.61c	13.45a	8.01b	5.95c	11.17c	14.31a
Control	0–1	0.52	11.84	6.73	6.35	10.35	16.21
Native	—	0.47	13.15	6.73	6.35	8.55	16.75
Soil 2							
Spiked sewage sludge	0–1	20.35a	62.71a	87.65a	350.56a	11.48a	247.25a
	1–2	10.93a	57.15a	47.65b	50.51b	9.41a	103.35b
	2–3	9.45a	20.15b	19.97b	18.92b	8.91a	5.37b
Sewage sludge	0–1	2.87a	15.98a	18.49a	8.45a	8.77a	4.43
	1–2	2.45b	14.46a	14.05a	6.35a	7.65a	9.52
	2–3	2.21c	9.08a	12.61a	5.99a	7.08a	14.03
Control	0–1	2.43	11.09	9.58	7.51	9.15	10.25
Native	—	2.65	7.32	9.25	7.52	13.85	16.41
Soil 3							
Spiked sewage sludge	0–1	14.38a	122.29a	81.28a	278.75a	154.21a	249.09a
	1–2	10.66b	15.49b	20.31b	25.48b	10.06b	1.98b
	2–3	7.61b	9.67b	19.84b	19.53c	7.81b	1.17b
Control	0–1	0.01	12.24	7.15	7.45	11.32	7.82
Native	—	0.45	6.59	7.13	7.42	12.75	11.65
Soil 4							
Spiked sewage sludge	0–1	13.33a	240.75a	67.22a	509.61a	20.31a	123.79a
	1–2	8.73b	24.07b	24.46b	47.52b	12.12b	21.83b
	2–3	2.19c	11.83c	17.72b	16.03b	7.12c	8.84c
Control	0–1	0.67	9.04	10.35	14.06	15.36	32.52
Native	—	0.82	6.35	7.12	14.05	13.31	40.35

Values within a column followed with the same letter are not significantly different at the 0.05 probability level.

application of spiked sewage sludge significant amounts of Cd remained in the CARB, EXCH and MNO fractions that could maintain Cd in a labile chemical form and may be more readily available to plants. Thus, in the soil leached with spiked sewage sludge, most of the added Cd was present in the CARB and EXCH fractions, with the fraction distribution being CARB > RES > EXCH> MNO > FEO > OM, whereas in soil leached with sewage sludge, the order was CARB > EXCH > MNO > OM > FEO > RES. For soils polluted by smelter dust, Xian (1989) reported that the largest amount of Cd was found in the EXCH

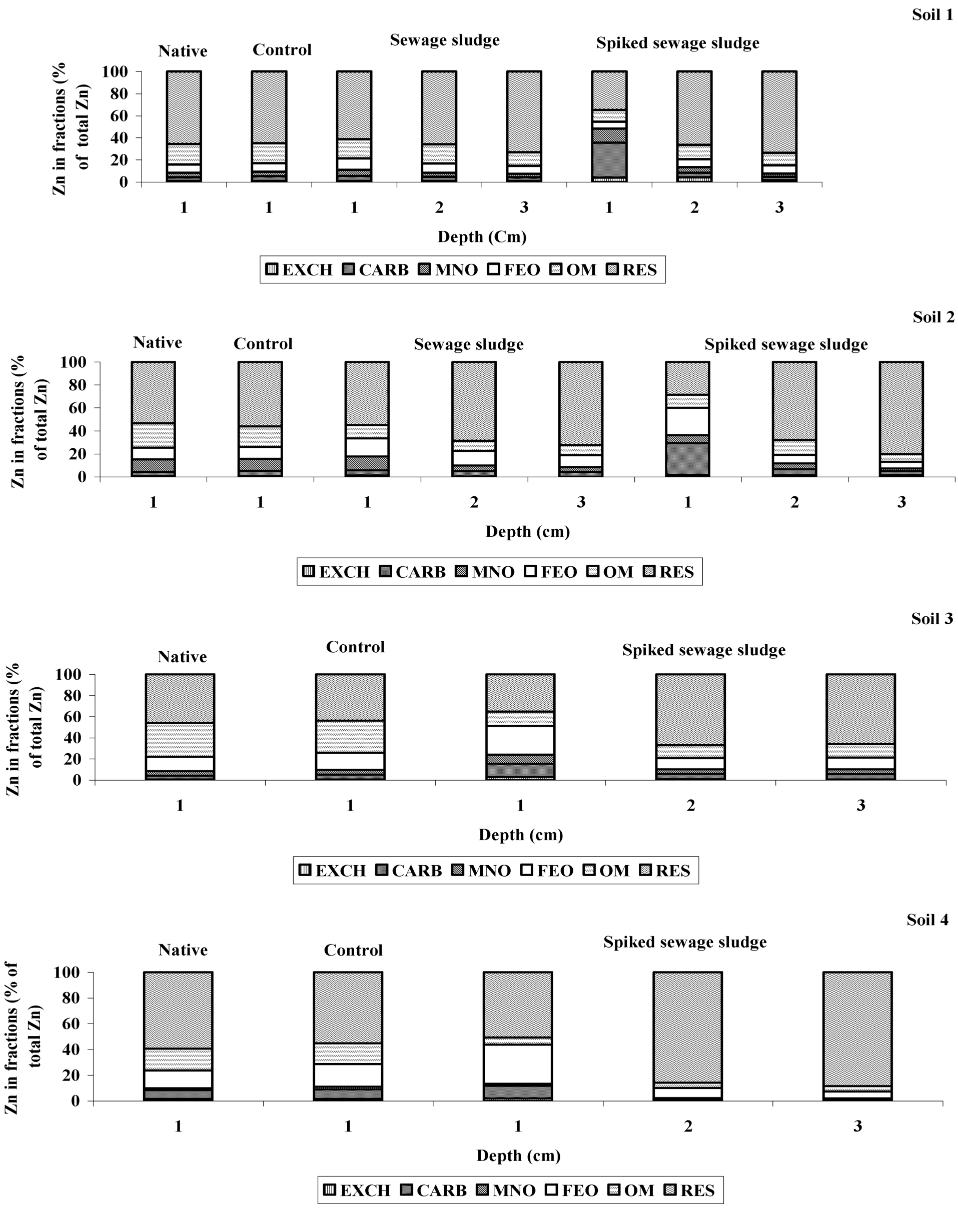

Figure 4. The proportional percentage of Zn in fractions of soils in spiked sewage sludge treated soil columns in three depths at the end of leaching experiment.

fraction. Also, Berti and Jacobs (1996) found that the greater percentage of soil Cd was in the EXCH fraction.

The proportion of Pb associated with the CARB, FEO and RES fractions, in all three layers was greater than the other fractions in soil leached with spiked sewage sludge. Similar to Zn, the RES fraction was the most important fraction for Pb in all treated soils, ranging from 31.7% (sewage sludge spiked) to 17% (sewage sludge) in the 0–1 cm soil layer (Figure 6). The FEO and MNO fractions contained most of the Pb in the nonresidual

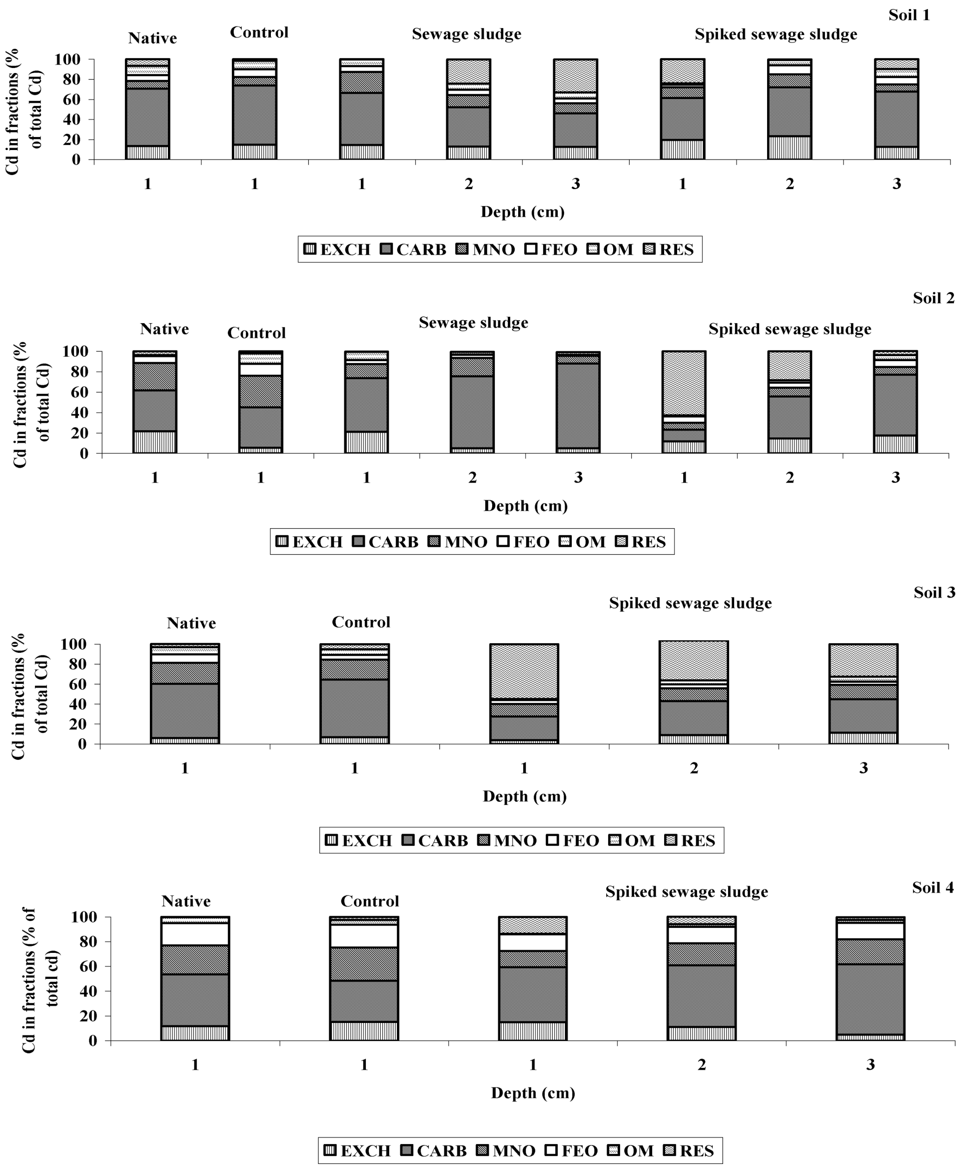

Figure 5. The proportional percentage of Cd in fractions of soils in spiked sewage sludge treated soil columns in three depths at the end of leaching experiment.

fractions and ranged from 23% in spiked sewage sludge soils treatment to 19.9% in sewage sludge treatment. The result was in agreement with those of Zhu and Alva (1993), Zhang *et al.* (1997), and Zinati *et al.* (2004) that with pH > 7.4, Pb in Fe-Mn oxides form was greater proportion in Florida soils than other fractions. The dominating fraction for Pb was FEO (26.5%) in soils leached with spiked sewage sludge. Lead in each fraction were generally in the order FEO > CARB > MNO > RES > OM > EXCH, while in soils leached with sewage sludge, the order was CARB > RES > OM > MNO > FEO > EXCH.

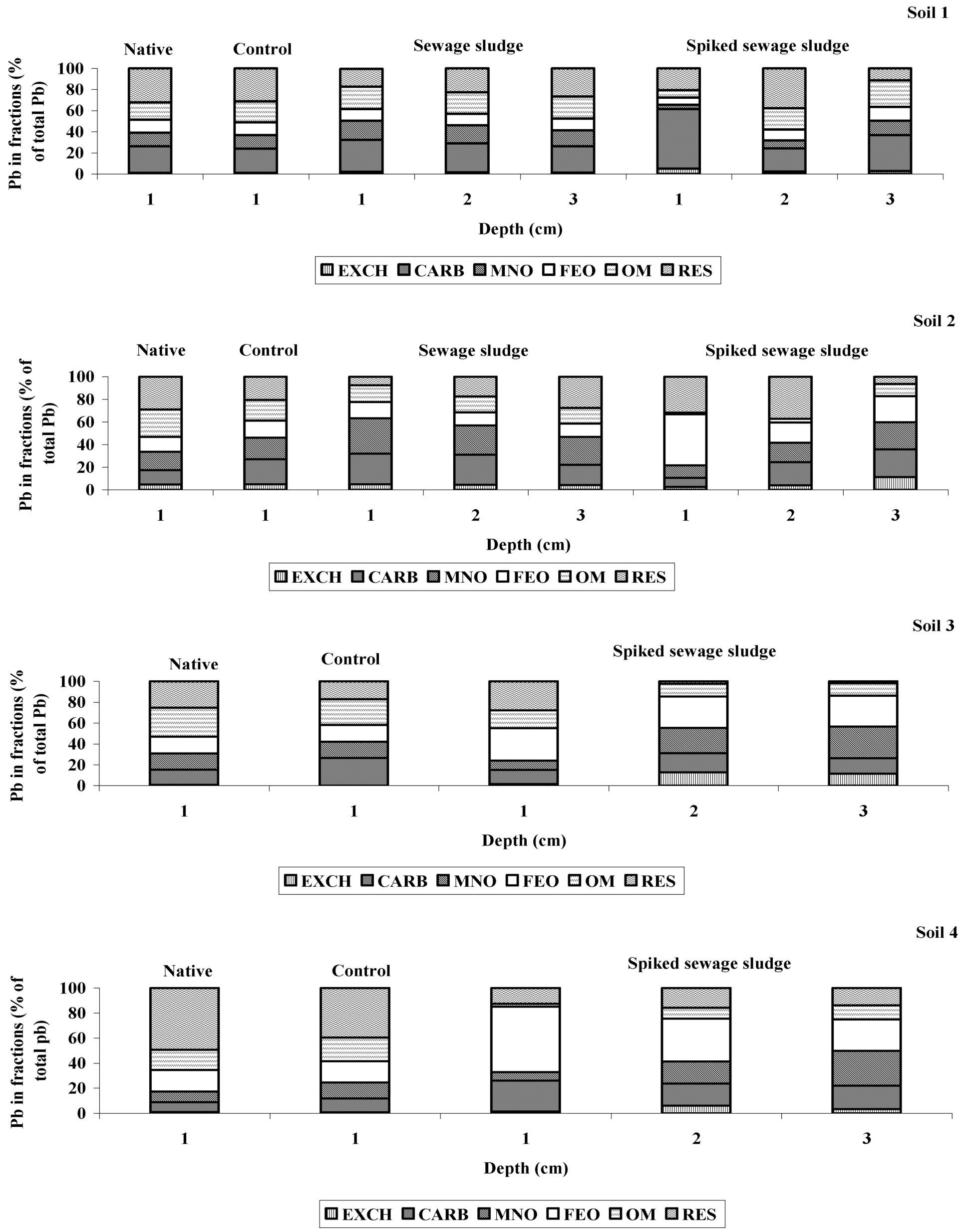

Figure 6. The proportional percentage of Pb in fractions of soils in spiked sewage sludge treated soil columns in three depths at the end of leaching experiment.

Xian (1989) found that the organic fraction was higher than the other fractions of Pb in sewage sludge acid amended soils. But in soil leached with sewage sludge, the dominant fractions were RES, CARB and MNO. Sposito *et al.* (1983) found that Pb was mostly present in inorganic and RES fractions.

In the 0–1 cm soil layer, the proportions of the metals in the EXCH and CARB fractions followed the order Cd > Pb > Zn. Several studies have reported that Cd is the most mobile heavy metal in soils and that a large part is associated with the readily leached EXCH and CARB fractions (Harrison *et al.*, 1981; Chlopecka *et al.*, 1996). These results suggest that the anthropogenic Cd was weakly adsorbed, probably to the negatively charged sites of clay and organics. Cadmium from anthropogenic sources tend to be more mobile than pedogenic or lithogenic ones (Kuo *et al.*, 1983). This loosely bound Cd may be desorbed and re-entered the aqueous phase by complex equilibrium reactions or by mass action of more abundant cations. This means that at least some of the retained Cd may become a secondary source of metal pollution.

Conclusions

The addition of either sewage sludge or spiked sewage sludge to the leaching columns containing calcareous soils of western Iran yielded greater concentrations of total Zn, Cd and Pb in the surface soil layer than in the adjacent and deeper soil layers (0–3 cm). The results suggest that applying either sewage sludge or spiked sewage sludge to calcareous soils the Zn, Cd and Pb was partitioned predominantly in the RES form, followed by the Fe-Mn oxides form, cadmium was an exception, with Cd accumulating mainly in the Fe-Mn oxides form, followed by the RES and CARB forms. These findings suggest that Zn, Cd and Pb were held in a more stable form (RES form) in which the movement of these elements in the soil profile would be negligible. These calcareous soils are able to retain Zn, Cd and Pb from spiked sewage sludge and the amounts of heavy metals adsorbed varied with soil types. The highest metal concentrations were found at the surface soil (0–3 cm) of the treated soil columns and decreased with depth. The vertical movement of the retained heavy metals also depended on soil types; relatively less downwards migration was found in Kabodar ahang than the other soils. Most of the applied heavy metals retained in the surface soil were bound in the RES, CARB and OM fractions. The percentages of Zn, Cd and Pb bound in the EXCH fraction of the spiked sewage sludge soils increased, suggesting that a portion of the retained metals might be released back to the aqueous phase and become secondary source. Among these heavy metals investigated, Pb from anthropogenic source was more permanently bound. These results suggest that the adsorption and the retention mechanisms of heavy metals varied with calcareous soil types and metal species.

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