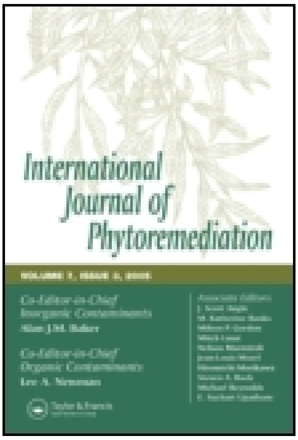

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EFFECTS OF PHYTOREMEDIATION AND APPLICATION OF ORGANIC AMENDMENT ON THE MOBILITY OF HEAVY METALS IN A POLLUTED SOIL PROFILE

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This research aims to assess the effect of the application of biosolids compost and phytoremediation on the mobility of total and biodisponibles (DTPA) fractions of cadmium, copper, lead, and zinc from different horizons of a superficially contaminated soil. Leaching experiment in soil columns was proposed. Treatments contemplated application of compost biosolid and phytoremediation. Two destructive samplings were performed. Total and DTPA trace metals were identified in each horizon. The overall performance of the various elements in its total and DTPA forms show greater concentration in horizon A and fewer gradients between horizons Bt and BC, thus assuming that the high content of clay in horizon Bt (62.9%) limits its movement through the horizons. In the mobile nutrients, a greater mobility was evidenced in DTPA fractions if compared to Total fractions. In the horizon A, the more mobile metals, such as Zn and Cd, evidenced a greater percentage of DTPA/Total fractions in all treatments. The application of compost with or without plant diminished the mobilization of Zn, Cu, and Cd Total, thus limiting a potential leaching to inferior horizons. However, this effect was not observed in the DTPA fraction.

KEY WORDS: biosolid compost, Cd, Cu, Pb, Zn

INTRODUCTION

Heavy metal contamination in agricultural soils is a crucial environmental problem that can reduce plant productivity and safety regarding the production of food (Alloway 1995; Kabata-Pendias and Pendias 1991).

The quality of metal-polluted soils is generally based on the total metal concentrations found in the soil. Although it is useful to determine the general level of soil pollution, total metal concentrations do not explain their bioavailability or their real toxicity per se. Soil characteristics are the most important factors influencing their bioavailability (Lukkari et al. 2004). Metal extraction with DTPA (Diethylenetriamine Pentaacetic Acid) provides the chemical evaluation of the number of metals that can be absorbed by vegetables (Hernández et al. 1991; Obrador et al. 1997; Petruzzelli 1989; Su and Wong 2003).

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The use of leaching column experiments as a tool to evaluate metal mobility in the soil is increasing (Anderson et al. 2000). This method can be applied to determine the effect of different practices regarding metal mobility and bioavailability (Cukrowska et al. 2004).

Among said practices, it is worth mentioning the phytoremediation, an environmentally acceptable technology that uses plants to remedy soils polluted with trace elements. The proper selection of vegetal species plays a vital role in the development of remediation methods (decontamination or stabilization), especially in soils with low or medium pollution levels (Salt et al. 1995). On the other hand, the application of organic amendments in situ has been used to reduce metal bioavailability of soils. The main objective of amendment application is to reduce metal bioavailability, while not affecting total concentrations (Brown 2005). However, in some other occasions, these amendments can also add soluble organic ligands which have the property of increasing metal mobility and leaching underground water (Shuman 1998).

This research aims at evaluating the effects of the application of biosolid compost and the phytoremediation on the mobility of total and DTPA fractions of cadmium, copper, lead, and zinc through the different horizons of a superficially polluted soil.

MATERIALS AND METHODS

Obtaining and Polluting Soil Samples

The horizons A, Bt, and BC of a Typical Argiudol located in San Antonio Areco, province of Buenos Aires, were obtained. Their main characteristics are included in Table 1. Horizon A was enriched with Zn, Cu, Cd, and Pb nitrate solutions. Polluted soils were moistened according to field capacity and they were air-dried in cycles of approximately 15 days within a 3-month period in order to reach equilibrium with soil colloids (Martínez and Motto 2000).

Leaching Experiment in Soil Columns

PVC columns of 0.15 m of diameter were used with three different heights: 0.20, 0.35, or 0.48 m. Heights were established according to horizon A (0.12 m horizon A), horizons A + Bt (0.12 m horizon A and 0.15 m horizon Bt), and horizons A + Bt + BC (0.12 m horizon A, 0.15 m horizon Bt, and 0.13 m horizon BC), respectively. The treatments were: 1) sample (polluted soil); 2) polluted soil + plant (Plant); 3) soil + 50 tn ha^{-1} soil compost (Compost), and 4) polluted soil + 50 tn ha^{-1} compost + plant (Compost-Plant). The cultivation used was *Festuca rubra*. It was designed as a random block test with three repetitions per treatment. The compost was prepared with sawdust as the structuring material, and biosolids (1:1, v:v) obtained in the sewage treatment plant located in San Fernando, province of Buenos Aires. The physical, chemical, and biological properties of the compost were previously published (Zubillaga and Lavado 2003). It should be pointed out that the contents of heavy

Table 1 Main characteristics of the studied horizons

	CO (%)	pH	Clay (%)	Silt (%)	Sand (%)	Texture
A	2.02	5.8	31.3	57	11.7	Loamy clayey-silty
Bt	0.83	6.3	62.9	28.3	8.8	Clayey
BC	0.21	6.7	42.3	46.8	10.9	Clayey-silty

metals were below the limits established by the Argentine regulations (MDSMA 2001), and even the contents of Cd were below the analytical limit used.

Two destructive samplings were performed in the columns: one after two harvests and two leachings, and the last one, after four harvests and leachings. Leachings were collected after incorporating the following volumes of water to column A: 1000 mL, A + Bt: 1200 mL, A + Bt + BC: 2000 mL. Due to the irrigation control, no leachates were produced among samples. Harvests were performed every 7–8 weeks. Data is presented as a concentration and as the contents obtained due to the concentration data and the soil mass of each horizon.

Analytic Determinations and Data Processing

Cd, Cu, Pb, and Zn-Total were determined by regal water absorption (nitric acid, hydrochloric acid, and sulfuric acid, McGrath and Cunliffe 1985) and availability (extraction with DTPA, Sparks et al. 1996). Soil extracts were determined with ICP (spirometric technique of plasma).

All data was statistically analyzed through the analysis of variance (ANOVA), and the difference among means was taken with the reliable differences test (LSD, $p < 0.05$). Relations among variables were established with the statistic program Table Curve (Jandel 1992).

RESULTS AND DISCUSION

Metal Total Concentration and Availability in the Different Horizons of Soil

In general terms, both sampling moments evidenced that the concentration of horizon A was greater than those of Bt and BC, with certain differences among the treatments. This applied to all elements, both in their total and available forms (Figure 1). This is due to the superficial pollution, as well as to the fact that, under pH conditions, clay contents and organic matter of sample, the mobility of elements is limited. According to Udom et al. (2004), heavy metals such as zinc, lead, cadmium, and copper, added to the soil through the biosolids, are accumulated from the surface up to 65 cm depth. On the other hand, it could also be caused by the fact that the leaching diminished the concentration of elements in successive horizons.

In general terms, horizon A evidenced that, when applying compost, the total concentrations of mobile elements, such as Zn and Cd, regarding Control and Plant were greater after both samplings. This could be due to the fact that the applied compost inhibited Cd and Zn fractions, whereas the decrease observed in the Plant treatment could have been caused by the cultivation absorption. When Zn measurements were taken in the leachates (Zubillaga and Lavado 2006), a smaller Zn concentration was observed in leachates with certain remediation treatment regarding Control, in the majority of columns and leachings. Said concentrations diminished in successive leachings.

Regarding metals with low mobility, such as Pb and Cu, it was observed that no differences were found between treatments, both in their total and available forms. Due to the low mobility of Pb in soils (Fischerováa et al. 2006), high concentrations of Pb-Total were observed in horizons Bt and BC. Pb-DTPA fractions in horizon A were greater than those of the rest of the horizons. There is no bibliographic information that can explain the

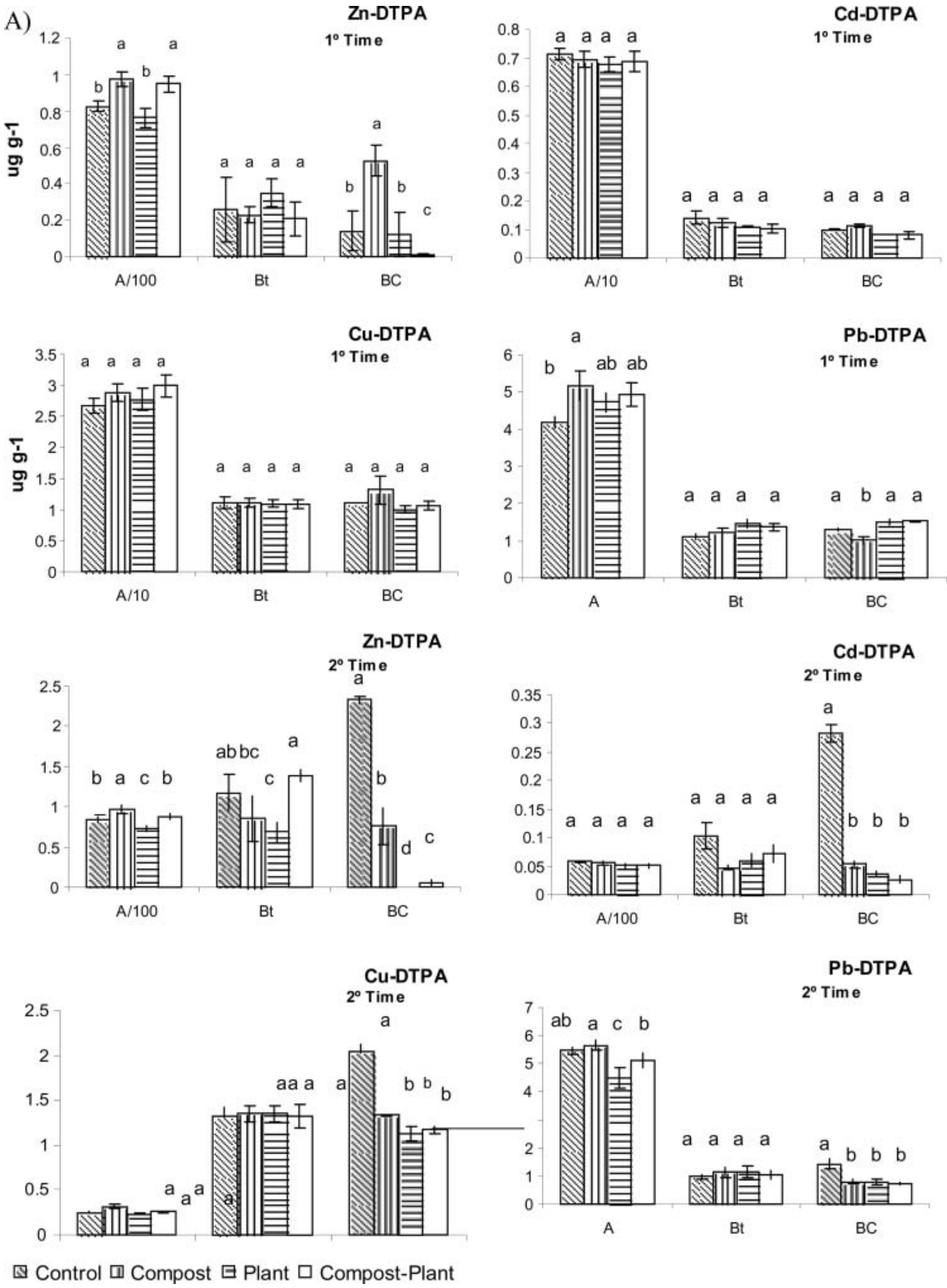

Figure 1 Concentration of Zn-DTPA (A) and Zn-Total (B) in the different moments of the leaching process for each treatment. The bars indicate a standard mistake, whereas the letters indicate the significant differences among treatments for each horizon. *(Continued)*

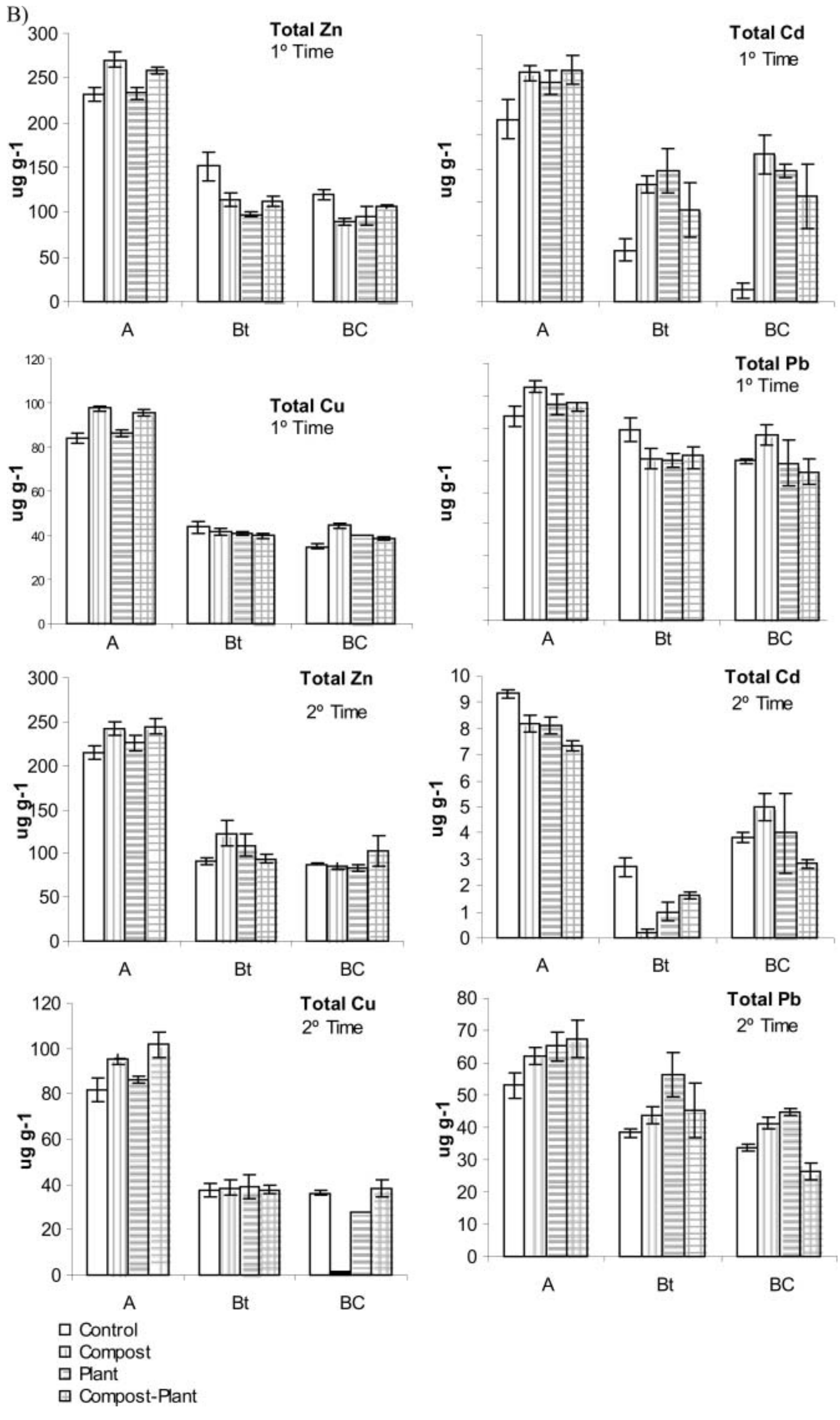

Figure 1 (Continued)

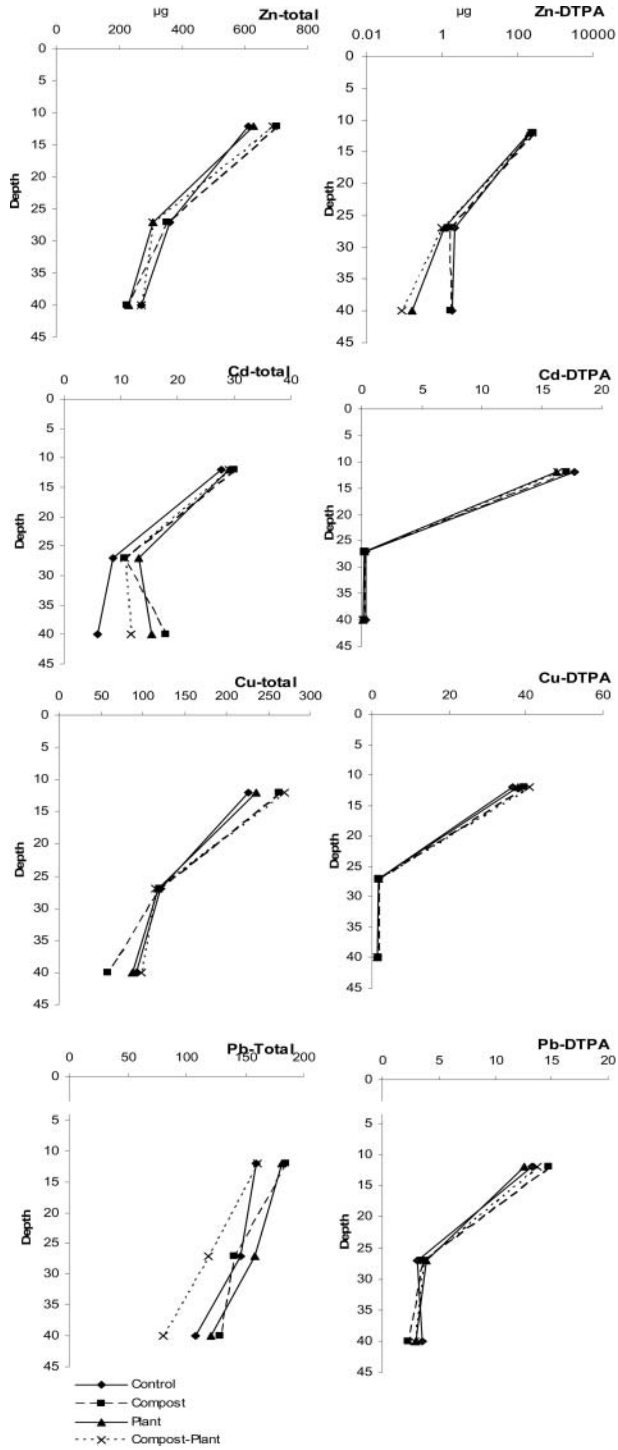

Figure 2 EPT-Total and EPT-DTPA contents of both leachings, in the different soil horizons.

Table 2 % EPT-Total/EPT-DTPA for each element and depth

	Control	Compost	Plant	Comp.-Plant
Zn				
A	37.32	37.79	32.62	36.66
Bt	0.59	0.46	0.36	0.32
BC	0.66	0.74	0.07	0.03
Cd				
A	63.82	57.24	55.90	56.13
Bt	4.20	2.36	1.92	1.94
BC	5.89	1.20	0.99	1.16
Cu				
A	16.15	14.94	16.11	15.19
Bt	1.37	1.38	1.38	1.41
BC	1.56	2.89	1.49	1.39
Pb				
A	8.29	8.03	6.96	8.58
Bt	2.14	2.51	2.45	3.04
BC	3.29	1.82	2.45	3.63

behavior detected in this case under study. In the first leaching, Cu-DTPA and Cu-Total contents were greater in horizon A. This allow confirming that copper is a metal with limited mobility, which is accumulated in the surface of polluted soils (McLaren and Crawford 1973), although successive leachings allow the movement of the DTPA fraction.

Metal Total Mass in the Different Horizons of Soil

The total and DTPA content of metals in the different horizons of soil is show in Figure 2, which represents the sum of both sampling moments. The general behavior of the different elements, both in their total and DTPA forms, evidence greater concentration in horizon A and less gradient between horizons Bt and BC, thus assuming that the high content of clay in horizon Bt (62.9%) limits its movement through the horizons. This was proven by the leachings obtained from said horizons (non-submitted data). Pb-Total differs from this general rule, as despite being a nutrient with low mobility, no strong gradients were found between the total contents of horizons A and Bt. Table 2 shows the variation percentage of DTPA fractions if compared to the variation of the Total fractions in horizons A and BC. In the mobile nutrients (Zn and Cd), a greater mobility was evidenced in DTPA fractions if compared to Total fractions.

As regards the differences among treatments, these were greater in the total fraction. The differences among treatments were variations between the different metals and their fractions. The Zn Total and the Cu Total evidenced a similar behavior. Fewer contents were

Table 3 % DTPA A -DTPA BC/Total A -Total BC for each treatment

	Control	Compost	Plant	Comp.-Plant
Zn	66.19	55.45	51.61	60.44
Cd	79.26	141.00	117.21	94.25
Cu	26.16	18.44	24.73	23.16
Pb	18.75	22.33	16.12	13.54

found in the Control and Plant treatments of horizon A. In the Plant treatment, this smaller concentration could have been caused by the cultivation absorption. Thus, it is observed that the application to the different treatments had a significant effect in the retention of Zn Total. In the Cd Total, the Control treatment had fewer total contents if compared to the other treatments. This suggests that the effect of limiting Cd mobility with the application of the different remediation treatments was positive. Regarding Pb Total, the different horizons evidenced a greater mobility of the Compost-Plant treatment. No significant differences were observed among the treatments in Cd, Cu, and Pb Total.

Table 3 shows the percentage of DTPA fraction if compared to the Total fraction. In the horizon A, a greater relation was observed for all the analyzed metals if compared to the other horizons. In the horizon A, the more mobile metals, such as Zn and Cd, evidenced a greater percentage of DTPA/Total fractions in all treatments if compared to the less mobile metals, such as Cu and Pb. Uneven behaviors were observed in the other horizons, although Zn had less relation than the rest of the metals.

CONCLUSIONS

The results of the experiments in columns help clarifying the effect of adding biosolid compost and of phytoremediation in a soil polluted with trace metals. It is worth pointing out the mobility of DTPA fractions if compared to Total fractions.

The relations between DTPA and Total fractions were greater in horizon A, mainly among more mobile metals.

The application of compost with or without plant diminished the mobilization of Zn, Cu, and Cd Total, thus limiting a potential leaching to inferior horizons. However, this effect was not observed in the DTPA fraction.

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