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Heavy Metal Mobility in Polluted Soils: Effect of Different Treatments

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Abstract: The effects of biosolid compost and phytoremediation applied on the leaching of cadmium, copper, lead and zinc, through the different horizons of a superficially polluted soil were determined. The soil was from the Province of Buenos Aires, Argentina. It was contaminated with cadmium copper, lead and zinc. Leaching columns were used with three different horizons: A: 0.12 m A horizon, B: 0.12 m horizon A+0.15 Bt horizon and C: 0.12 m A horizon+0.15 m Bt horizon+0.13 mBC horizon. The treatments were (1). Witness (contaminated soil), (2). contaminated soil+plants (Plant), (3). contaminated soil+50 Mg has^{-1} biosolid compost (Compost) and (4). contaminated soil+50 Mg has^{-1} biosolid compost+plants (Compost-Plant). The leached ones were gathered after incorporating to the columns the following volumes of water A: 1000 mL, B: 1200 mL and C: 2000 mL. Leachates were obtained out after harvesting vegetal material. It was found that horizon Bt presents a barrier to metal leaching. Both concentration of clay and type of clay appears to immobilize heavy metals in those soils. The clay content over 40% and/or 53.4 g smectite g^{-1} soils reduce the heavy metal leaching. The application of organic amendment or occurrence of plant eventually used in remediation techniques did not influence on the leaching of metals.

Key words: Biosolid compost, fitoremediation, leaching, texture

INTRODUCTION

The deposition of industrial waste, mining activities, incidental accumulations, atmospheric deposition, agricultural chemicals, etc., are some sources for the pollution of soils with heavy metals [1]. The mobile forms of those heavy metals constitute a risk as they may leach into groundwater that could be later used for human or animal consumption[2]. Soil pH, other factors such as the presence of competing ligands, the ionic strength of the soil solution and the simultaneous presence of competing metals are known to significantly affect sorption processes and leaching potential through a soil profile[3]. The absorption of heavy metals differs in the different soil horizons, due to texture composition in different soil horizonts.

In order to avoid the accumulation of metal and their movement within soil profile, different remediation techniques were developed. Among them those based on adding materials capable of immobilizing mobile forms of metals [4,5], like compost and biosolid are adequate[6] are adequate. Another technology is the phytoremediation, based on the absorption of heavy metal by different plant species, which latter are removed[7]. Perez-de-Mora *et al*.[8] found that the use of amendments (like biosolid compost) and plant cover was important for in situ remediation of heavy metal contaminated soils.

Our objective was to evaluate the effects of biosolid compost and phytoremediation separate or simultaneously applied on the leaching of cadmium, copper, lead and zinc, through the different horizons of a superficially polluted soil.

MATERIALS AND METHODS

The horizons A, Bt and BC of a Typical Argiudoll located in the province of Buenos Aires (34°8’ S, 59°4’ W), Argentine were collected. The soil main characteristics are included in Table 1. Mineralogy values obtained by[9] in nearby Tipic Argiudolls are present (X-ray decomposition Program, DECOMPXR)[10]. The horizon A was enriched with cadmium copper, lead and zinc applied as nitrate. The polluted soils were moistened to field capacity and allowed to dry in cycles of approximately 15 days within a 3-month period in order to reach equilibrium with soil colloids[11].

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Table 1: Main characteristics of the studied horizons. S = Smectite, I = Illite, I/V = Interstratified illite-vermiculite. The relative proportion expressed in area percentage in diffraction diagrams were after Castiglione *et al*.[9]

Soil Horizons	OC (%)	pH	Clay (%)	Silt (%)	Sand (%)	Mineralogy S	Mineralogy I+I/V	Texture
A	2.02	5.8	31.3	57	11.7	44	53	Loamy clay-silty
Bt	0.83	6.3	62.9	28.3	8.8	64	33	Clayey
BC	0.21	6.7	42.3	46.8	10.9	81	18	Clayey-silty

Table 2a: Main characteristics of the biosolidcompost. CEC, capacity exchangeable cationic, TC, total carbon, SC, soluble carbon, TN, total nitrogen, HA, humic acid, FA, fulvic acid, IL, ignition losses, DM, dry matter

pH (1:5)	CEC $cmol_c\ kg^{-1}$	TC	SC	TN	HA	FA	IL	DM
		------- $g\ kg^{-1}$	--------		---------------	%	-------------	
6.9	16	4.2	0.03	0.44	0.5	0.3	41	65

The soils were put in PVC tubes (0.15 m diameter) of three heights. Columns of 0.20 contained 0.12 m A horizon (A), columns of 0.35 contained 0.12 m A+0.15 m Bt horizon (B) and columns of 0.48 m contained 0.12 m A+0.15 m horizon Bt+0.13 m horizon BC (C).

The treatments were: 1) polluted soil (control), 2) polluted soil+plant (Plant), 3) polluted soil+50 Mg biosolid compost ha^{-1} soil (Compost) +50 Mg biosolid compost ha^{-1} +plant (Compost-Plant). The plant used was *Festuca rubra*. The experiment 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. Its most relevant characteristics are shown in Table 2a.

Leachates were collected after adding water to columns: A: 1000 mL, B: 1200 mL, C: 2000 mL. Leachates were obtained out after harvesting vegetal material, every 7-8 weeks, totaling 4 leachings. No leachates were produced between sampling. Cadmium, Cu, Pb and Zn were determined using plasma emission spectrometer technique (ICP)[12].

Data are presented as a concentration of metals and as a total mass of leached metals. It was calculated by multiplying concentration and the volume of leachate divided by the volume of water that entered each column. All data were statistically analyzed through the analysis of variance (ANOVA) and the difference among means was checked with the least significant differences (LSD, $p<0.05$).

RESULTS AND DISCUSSION

The content of heavy metals in the compost (Table 2b) was below the limits established by the Argentinean regulations[13]. Therefore, there would be no significant heavy metal addition in treatments using compost.

Table 2b: Heavy metals in biosolid compost, $mg\ kg^{-1}$

Ni	Ba	Cr	Cu	Zn	Pb	Hg	As	Ag	Se	Cd
109	443	230	727	1183	383	4.3	17	21	<7	<4

The impact the treatments had on the leachates obtained from the soil columns is showed in Table 3. There was a general variability of concentrations within each treatment, which caused the lack of significant differences among them. However, in the treatment compost, Cd concentration in some leachings of columns whit A and C horizons were significantly higher ($p<0.05$) if compared to the Control. Besides, in Control, there was a significant increase of Cd concentrations ($p<0.05$) in successive leachings. Antoniadis and Alloway[14] observed that the application of an organic waste in polluted soils increased Cd concentrations in leachates. This is possibly due to the formation of complexes with soluble fractions of organic matter. Even though the concentration of Soluble Organic Carbon (SOC) of the compost used was low[15], Table 2, it could cause of the increase in Cd solubility, thus favoring its movement within the columns.

Copper concentration increased significantly ($p<0.05$) in the first leachate of A column, in the Compost-Plant treatment. Cu concentrations diminished considerably ($p<0.05$) in the successive leachings of all treatments with compost and compost-plant. Gove *et al*.[16] observed in soil columns of 0.40 m that losses due to leachings were generally greater during the first leachings, thus assuming that there was a partial decrease of Cu in the labile pool.

Lead concentrations were not affected in general terms by the treatment. This could be accredited to the low solubility of Pb in the soil[17]. Zinc concentrations in the leachates diminished significantly ($p<0.05$) when compared Plant treatment to the Control in certain columns and leachings.

The mass of leached metals of each treatment is showed in Fig. 1. In general terms, the same leaching pattern was observed in the four analyzed metals and in all treatments. There was a greater mass of heavy metals in the leachates in A column, if compared to B and C columns. No significant variation was found into B and C columns. Horizon Bt, with 62.9% of clay, presents evidently a barrier for the passing of metals, and caused a true abrupt reduction of the total mass of leached metals. Due to their high specific surface, clay minerals play an important role in the immobilization of heavy metals through the superficial complexion

Table 3: Average concentrations of Cd, Cu, Pb and Zn among the four leachings collected in the different columns, mg L^{-1}. 1º letter: Significant differences within leachings, 2º letters: Significant difference within treatment. Values followed by the same letter do not differ significantly ($p<0.05$)

Columns	Leachings	Control		Compost		Plant		Compost-plant	
Cd									
A	1	0.01327	a-ab	0.00613	b-b	0.00833	ab-b	0.02047	a-a
	2	0.00220	b-b	0.00453	b-a	0.00133	b-b	0.00173	c-b
	3	0.00787	a-ab	0.01027	a-a	0.00900	ab-ab	0.00540	b-b
	4	0.01027	a-ab	0.00840	a-ab	0.00627	ab-b	0.00667	b-b
B	1	0.00024	b-nd	0.00156	b-nd	0.00045	b-nd	0.00120	b-nd
	2	0.00093	b-nd	0.00264	b-nd	0.00040	b-nd	0.00127	b-nd
	3	0.00773	a-ab	0.00747	a-a	0.00693	ab-ab	0.00580	a-b
	4	0.00648	a-nd	0.00707	a-nd	0.00627	ab-nd	0.00360	b-nd
C	1	0.00000	c-b	0.00100	c-a	0.00053	b-ab	0.00040	b-ab
	2	0.00112	bc-ab	0.00033	c-b	0.00040	b-b	0.00007	b-b
	3	0.00208	ab-c	0.01587	a-a	0.00720	ab-b	0.00453	a-bc
	4	0.00320	a-nd	0.00680	b-nd	0.00000	b-nd	0.00180	ab-nd
Cu									
A	1	0.01760	nd-b	0.02590	a-b	0.02367	a-b	0.04760	a-a
	2	0.00807	nd-nd	0.00600	b-nd	0.01360	a-nd	0.00650	b-nd
	3	0.00880	nd-nd	0.00533	b-nd	0.01573	ab-nd	0.00720	b-nd
	4	0.00880	nd-nd	0.00560	b-nd	0.00227	b-nd	0.00533	b-nd
B	1	0.00760	a-nd	0.01364	nd-nd	0.01505	nd-nd	0.00500	nd-nd
	2	0.00573	a-nd	0.00360	nd-nd	0.00648	nd-nd	0.00573	nd-nd
	3	0.00747	b-nd	0.00240	nd-nd	0.00547	nd-nd	0.00520	nd-nd
	4	0.00320	ab-nd	0.00540	nd-nd	0.00120	nd-nd	0.00347	nd-nd
C	1	0.00273	nd-nd	0.00273	nd-nd	0.00167	nd-nd	0.00133	nd-nd
	2	0.00533	nd-nd	0.00336	nd-nd	0.00610	nd-nd	0.00193	nd-nd
	3	0.00266	nd-nd	0.00600	nd-nd	0.00460	nd-nd	0.00533	nd-nd
	4	0.00040	nd-nd	0.00493	nd-nd	0.00000	nd-nd	0.00173	nd-nd
Pb									
A	1	0.00593	b-nd	0.00875	bc-nd	0.01013	b-nd	0.00873	nd-nd
	2	0.00000	b-b	0.00000	c-b	0.00633	b-a	0.00000	nd-b
	3	0.01280	a-nd	0.02267	a-nd	0.02987	a-nd	0.00920	nd-nd
	4	0.01680	a-nd	0.01360	ab-nd	0.01427	ab-nd	0.01387	nd-nd
B	1	0.00087	b-nd	0.00456	abc-nd	0.00875	b-nd	0.00060	b-nd
	2	0.00000	b-nd	0.00000	c-nd	0.00000	b-nd	0.00000	b-nd
	3	0.00980	a-nd	0.01320	a-nd	0.01773	a-nd	0.00533	a-nd
	4	0.01520	a-a	0.01253	ab-ab	0.00215	b-c	0.00640	a-bc
C	1	0.00000	b-nd	0.00000	c-nd	0.00000	b-nd	0.00000	b-nd
	2	0.00000	b-nd	0.00000	c-nd	0.00040	b-nd	0.00000	a-nd
	3	0.00000	a-nd	0.01700	a-nd	0.00920	a-nd	0.00307	b-nd
	4	0.01220	a-nd	0.01093	bc-nd	0.00000	b-nd	0.00000	b-nd
Zn									
A	1	0.73547	a-a	0.66155	a-a	0.44807	a-b	0.82760	a-a
	2	0.53000	b-ab	0.63967	ab-a	0.43920	a-b	0.40700	b-b
	3	0.11133	c-nd	0.09453	b-nd	0.13600	b-nd	0.08347	c-nd
	4	0.09920	c-ab	0.11400	b-a	0.06160	b-b	0.05333	c-b
B	1	0.65130	a-a	0.45444	a-ab	0.29398	a-b	0.48200	a-ab
	2	0.45800	b-a	0.41648	ab-a	0.34095	a-b	0.36580	b-b
	3	0.09453	bc-a	0.07900	ab-a	0.04693	b-b	0.04787	c-b
	4	0.03560	c-nd	0.05733	b-nd	0.06200	b-nd	0.04800	c-nd
C	1	0.18080	b-nd	0.34100	a-nd	0.28567	a-nd	0.26167	b-nd
	2	0.43900	a-nd	0.37776	a-nd	0.37153	a-nd	0.36050	a-nd
	3	0.08297	bc-b	0.08440	b-a	0.04340	b-b	0.05840	c-b
	4	0.02900	c-nd	0.08440	b-nd	0.04493	b-nd	0.04064	c-nd

effect[18]. Bt horizon with higher pH and clay content characterized by smectite (Table 1), respect to A horizon. B horizon, had the greatest metal sorption capacity due the presence of this clay mineral provides the soil with a large cation exchange capacity. Appel and Ma[19] observed that the presence of smectite as the dominant clay ensures high metal sorption capacity been a factor regulating the sorption of heavy metals by soils (Table 4). The BC horizon contains even more proportion of smectite than Bt horizon (Table 1), however its clay content is lower. In general, the B and C columns present the same leached metal content, reason why for this soil in study, the critical clay to limit the leaching are over 40% (Table 1). Considering

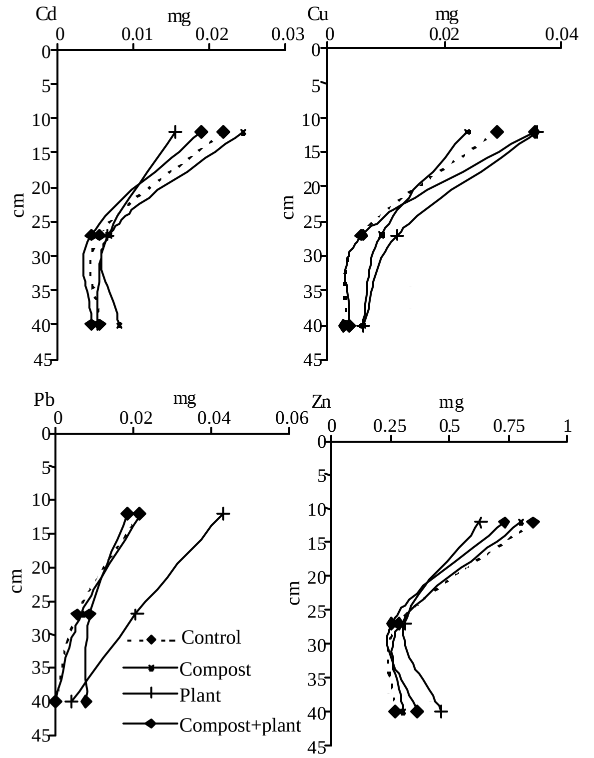

Fig. 1: Distribution of Cd, Cu, Pb and Zn leachates through the soil horizons

Table 4: Total heavy metals in the polluted superficial horizon and maximum limits accepted by regulations (mg kg^{-1})

	Total contents in the polluted horizon	Maximum limit as per the different regulations*
Cadmium	7.22	3
Copper	57.90	50
Lead	149.20	100
Zinc	166.40	150

*: Lower limits found in USEPA, CCE and other countries' guidelines[22]

the quality of clays this level critical is over 53.4 g smectite g^{-1} soils (value calculated with data Table 1).

In B columns, the mass of leached Cd was greater in Compost or Plant treatments if compared to the Compost-Plant treatment. In a soil column experiment, another authors[20,21] also observed that the presence of fescue or organic amendments increased Cd mobility. Copper showed a pattern similar to Cd, but no significant differences were observed among the treatments in any of the horizons. Pb evidenced a greater leached mass (d.s., $p<0.05$) in horizons A and B in Plant treatment. Zinc showed significant differences ($p<0.05$) only between Plant and Control treatments

Cadmium, Cu, Pb and Zn contents of the polluted soil horizon exceeded the limits established by international standards (Table 3). However, the concentration of those metals in the leachates from the different horizons evidenced that they scarcely exceed the limits established for the different uses of water[22].

CONCLUSION

This leaching experiment through the horizons of a typical soil of the Pampas region, showed that horizon Bt presents a barrier to metal leaching. Both concentration of clay and type of clay appears to immobilize heavy metals in those soils. The clay content over 40% and/or 53.4 g smectite g^{-1} soil reduce the heavy metal leaching. The application of organic amendment or occurrence of plant eventually used in remediation techniques did not influence on the leaching of metals.

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