



Journal of Applied Sciences

ISSN 1812-5654

science
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Contamination Time Effect on Plant Available Fractions of Cadmium and Zinc in a Mexican Clay Loam Soil

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Abstract: Knowledge of plant available fractions of heavy metals in soil can assist directing phytoremediation efforts for contaminated soils. For this reason different doses of ZnCl₂ (0, 200, 400 and 600 mg kg⁻¹) and CdCl₂, 2½ H₂O (0, 9, 18 and 27 mg kg⁻¹) were applied to an uncontaminated slightly acidic clay loam soil from State of Mexico, Mexico incubated under ambient temperature and humidity for 90 days. Both the metals were extracted with a DTPA-TEA-CaCl₂ mixture after 1, 5, 15, 25, 60 and 90 days and analyzed using atomic absorption spectroscopy. The results showed that DTPA extractable contents of Zn and Cd followed a decreasing trend with increase in incubation time. Maximum contents were found at day 01 in all the treatments. After 15 days of incubation, the variation in extractable contents was non-significant. The rapid adsorption of the metals might be due to elevated clay content (34%) of the incubated soil.

Key words: DTPA extractable Zn, cadmium, adsorption, plant available heavy metals

INTRODUCTION

An accurate description of the complex interactions of heavy metals in soils is a prerequisite to predicting their behaviour in the vadose zone. Specifically, to predict the fate of heavy metals in soils, one must account for retention and release reactions of the various species in the soil environment.

Heavy metals in soils can be involved in a series of complex chemical and biological interactions including oxidation-reduction, precipitation and dissolution, volatilization and surface and solution phase complexation (Selim and Amacher, 2001).

In the soil heavy metals may occur (1) on ion exchange sites (2) be incorporated into or on the surface of crystalline or non-crystalline inorganic precipitates (3) be incorporated into organic compounds, or (4) be in soil solution. Most researchers have recognized that heavy metals are sparingly soluble and occur predominantly in a sorbed state or as a part of insoluble organic or inorganic compounds. Due to low

solubility of the heavy metals in soils, their movement in soil profile has been considered usually small (Amaral Sobrinho *et al.*, 1998). The soil acts as a reservoir of heavy metals and also serves as a filter protecting the underground water against these metals thus contributing significantly to reduction of environmental contamination risks (Clarice de Oliveira *et al.*, 2003).

Zinc in soil that is water soluble and adsorbed on exchange sites of colloidal materials is considered to be phytoavailable. It is a consensus that phytoavailable Zn in soil can best be predicted by the use of extractants that remove only a fraction of the total amount. Despite its environmental and financial importance there is no agreement in the literature as to which extractant most accurately estimates the phytoavailability of trace metals in soils (Menzies *et al.*, 2007). More recently, the DTPA-extractable Zn has gained more attention as a diagnostic tool in the Zn nutrition of plants. Whether the soil is sludged (Bidwell and Dowdy, 1987; Bell *et al.*, 1991) or just ordinarily mineral arable soil (Singh *et al.*, 1987., Dang *et al.*, 1993), the DTPA is the extractant of choice.

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While a number of researchers have advocated the use of DTPA as an appropriate extractant (Sukkariyah *et al.*, 2005, Keller *et al.*, 2005; Nascimento, 2006, Zhang *et al.*, 2006) the others do not find it very useful for evaluating the bioavailability of metals (Basar and Aydinalp, 2005; Feng *et al.*, 2005; Ortiz and Alcaniz, 2006; Menzies *et al.*, 2007).

Ample literature on extractants used to measure phytoavailable Zn (e.g., salt solutions, acids, bases and chelates) exists. The needs vary by country, crop and soil type. A soil test using one of the extractants is done to (1) determine if the Zn level is sufficient and the soil requires no fertilization with Zn and (2) determine if the Zn level is excessive and will cause phytotoxicity, as in the case of sludged soils or soils heavily contaminated. In the latter case, management strategies should be part of any operational scheme, including adjustment of soil pH, adding amendments or selecting tolerant plant species (Adriano, 2001). Extractable Zn has been positively correlated with total Zn, organic matter, clay content and cation exchange capacity (Follet and Lindsay, 1970) and inversely correlated with free CaCO₃, soil pH and base saturation (Adriano, 2001).

On the other hand, special attention should be paid to Cd pollution in the soil-plant system, due to its mobility and the small concentration at which its toxic effect begins to show (Zornoza *et al.*, 2002). In most soils, more than 99% of the Cd content is associated with the solid phase and less than 1% is found in the soil solution. As Cd leachability and availability to plants conceptually are related to Cd in the soil solution and to pools of solid Cd that can be made available through the soil solution, it is mandatory to understand and quantify the solid phase Cd and the reactions and processes that govern the distribution of Cd between the solid phase and the soil solution. Adsorption is considered to be the dominating process governing Cd distribution between soil solid phases and the soil solution. The term adsorption accounts for the many different processes that may actively bind Cd to the solid phases of soils. Desorption describes the reverse process that releases Cd from the solid phases into the soil solution. The relationship between these two processes determines the distribution of Cd between the solid phases of the soil and the soil solution. Several factors related to the characteristics of solute can affect the actual distribution of Cd in the soil such as pH, cationic composition, competing trace metals and organic and inorganic ligands (Christensen and Huang, 1999).

Since the bioavailability of free metal in soil solution is regulated by the adsorption processes in organic and inorganic soil fractions, this study was aimed at understanding phytoavailability of soil Zn and Cd in

terms of their DTPA extractable contents in response to various doses of these metals applied to the incubated soil as influenced by time intervals.

MATERIALS AND METHODS

An unpolluted soil sample was obtained from the top 25 cm layer of a crop field at San Pablo Ixayoc, State of Mexico, Mexico (19° 23 43 and 19° 28 37 North and between 98° 42 51 and 98° 48 12 West). The soil was air dried, ground and passed through a 2 mm sieve and analyzed for its total Cd and Zn content and other physical and chemical properties (Table 1). The experiment was undertaken in April-June, 2006.

Unicel containers with 7 cm diameter were filled with 500 g of soil and incubated at ambient temperature and humidity. The temperature oscillated between 25 and 35°C during the course of experiment. The moisture level was maintained at 70% of soil water holding capacity and deficient water was replenished by weighing the containers every 2-3 days. Distilled water was used for this purpose. The experimental units were arranged in a randomized design with four treatments for each metal and three replications. The containers were re-randomized five times in the duration of the experiment. Zn was applied in the form of ZnCl₂ at the rate of 0, 200, 400 and 600 mg kg⁻¹ while Cd in the form of CdCl₂·2½H₂O at the rate of 0, 9, 18 and 27 mg kg⁻¹. The selection of the doses was based on the fact that in a previous study the same doses were applied to the soils used in this experiment for assessing Zn and Cd phytoextraction potential of *Lupinus uncinatus* Schldl. Zinc and cadmium were extracted with 0.005M DTPA, 0.1 M TEA and 0.1 M CaCl₂ (Soil Analysis-Hand Book of Reference Methods, 2000) in all the samples after 1, 5, 15, 25, 60 and 90 days of soil incubation with the metals. The concentrations of the two metals in the extract were analyzed using atomic absorption spectroscopy (Perkin-Elmer, 3110). The results were expressed on oven dry weight basis. Data were subjected to one-way ANOVA followed by a Tukey test for multiple comparison of means (Significance level p<0.05). All the statistical tests were performed using SAS (Statistical Analysis System) 9.1 version.

Table 1: Some physical and chemical properties of incubated soil

Parameter	Value	Method
pH	6.29	2:1 Water
EC	0.16 dS m ⁻¹	Conductivity meter
Organic matter	1.19%	Walkley and Black
Particle size distribution/	Sand (34%) Silt (32%)	
Soil textural class	Clay (34%/clay loam	Hydrometer method
Bulk density	1.05 g cm ⁻³	
Total Cd content	0.16 mg kg ⁻¹	AAS*
Total Zn content	65 mg kg ⁻¹	AAS

**Atomic absorption spectroscopy

RESULTS AND DISCUSSION

After incubation of different applied doses of ZnCl₂ for 1, 5, 15, 25, 60 and 90 days, the DTPA extractable Zn contents obtained are given in Fig. 1. Generally DTPA extractable Zn decreased with increase in incubation time. The magnitude of DTPA Zn was found proportional to the dose of metal applied to the soil. Maximum content was found at day 01 in all the treatments, followed by significant decrease at day 05 and day 15 while during the rest of the incubation period the difference in the DTPA Zn was non-significant statistically (p<0.05). These results suggest that Zn was sorbed by soil constituents rapidly as mentioned by Adriano (2001) who found that usual amounts of Zn applied were adsorbed almost completely within a short period of time. A similar decrease in DTPA extractable Zn was reported by Kandpal *et al.* (2004) who studied effect of metal spiking and incubation on sequentially extractable pools of various heavy metals. Romero *et al.* (2007) observed that adsorption and coprecipitation on Fe-precipitates played an important role in the mobilization and attenuation of Zn, Cd, Cu and As within the abandoned lead/zinc mine tailings in central-southern Mexico. Sorption of Zn in soils is an important factor governing Zn concentrations in soil solution and Zn bioavailability to plants. Clay minerals, hydrous oxides, carbonates, pH, cation exchange capacity, organic matter and soil type are known to affect soil sorption of added Zn.

Since the incubated soil had a high clay content (Table 1) and consequently high density of OH groups, favouring specific adsorption of Zn through covalent bonds (Clarice de Oliveira *et al.*, 2003). While studying the effects of soil properties on Zn adsorption, Shuman (1985) found that soils with high silicate clay content or organic matter possess high Zn adsorption ability as compared to sandy soils with low organic matter content.

Simple organic compounds such as amino acids and phosphoric acid as well as low molecular weight fulvic acid are efficient complexing and chelating agents of Zn, favouring its high mobility (Alloway,

1995), while the incubated soil in this study with low organic matter (Table 1) facilitated Zn adsorption.

While observing DTPA extractable Cd contents during the period of incubation (Table 2), a similar significant reduction in extractable Cd content was observed at day 05 followed by non-significant decreases until the end of the incubation period. Adsorption is the operating mechanism of the reaction of Cd at low concentrations with soils. Using loamy sand and sandy loam soils, sorption of Cd was demonstrated as a fast process where >95% of the sorption took place within the first 10 min and equilibrium was attained within an hour (Christensen, 1984). The presented data highlights one important fact that the plant available Cd content was highest during first five days after its application to the incubated soil. However a continuous decrease in DTPA extractable Cd was observed throughout the incubation period thus showing persistent soil sorption of the metal. Adriano (2001) enlists several factors which may influence the degree by which Cd is adsorbed on soil surfaces. Some of them are pH, ionic strength, exchangeable cations, competing trace metals, organic and inorganic ligands and natural properties of soil components. Gray and McLaren (2006) found that the importance of soil properties such as soil pH, total carbon and oxalate extractable Fe and Al oxides varied between heavy metals such as Ni, Cu, Cr, Pb, Cd and Zn. Metal solubility decreases in soil as the CaCO₃ content and soil pH increases while organic matter promotes the availability of metals by supplying complexing agents that interfere with the fixation of these metals (Mani and Kumar, 2005). Iron

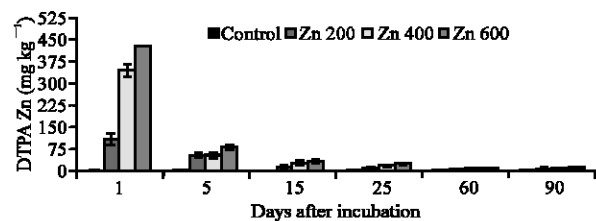


Fig. 1: Effect of various Zn doses on DTPA extractable Zn as influenced by time intervals

Table 2: DTPA extractable Cd at various time intervals in response to different doses of Cd applied to incubated soil. No in the same row followed by different letters differ significantly (p<0.05) according to Tukey test. Values within parenthesis represent standard deviation

Treatment (mg Cd kg ⁻¹)	Days after incubation					
	1	5	15	25	60	90
00	0.40a (0.06)	0.41a (0.06)	0.38a (0.09)	0.43a (0.06)	0.34a (0.05)	0.43a (0.05)
09	7.33a (0.57)	3.66b (1.15)	2.33bc (0.57)	2.33bc (0.57)	1.16c (0.76)	0.76c (0.25)
18	16.6a (2.51)	7.0b (2.00)	3.7bc (1.20)	3.0bc (1.00)	2.3c (0.60)	1.5c (0.40)
27	31.0a (3.00)	10.3b (2.10)	6.7bc (1.50)	6.0bc (1.00)	4.3c (1.50)	3.0c (0.20)

and manganese oxides and clay minerals like gibbsite, chlorite, smectite and goethite are the soil components with greater effect in the reduction of heavy metal availability (Vega *et al.*, 2004). The results obtained in the present study provide valuable information on metal availability in contaminated soils and offer an indication of the potential risk a metal may pose to a given soil environment, along with providing a basis for developing soil quality guidelines for the prevention, investigation and clean-up of soil metal contamination.

CONCLUSIONS

The accumulation of heavy metals in plants is related to concentration and chemical fractions of the metals in soils. Understanding chemical fractions and availabilities of the metals in soils is necessary for their management. The sorption-desorption behaviour of Cd and Zn assist prediction of their bioavailability and toxicity in the subsurface environment. The results from this study provided an insight into the plant available fraction of Cd and Zn over a 90 days incubation period and made a quantitative assessment of their soil mobility possible. Both the metals had maximum plant available content within 24 h of their application to the soil which decreased abruptly after this period. Hence these findings will be relevant to future research efforts on exploring the phytoremediation potential of some native plant species for such soils.

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