Bioavailability of cadmium and zinc following salinization of a degraded Isohyperthermic Arenic Kandiudult

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Abstract

This study was conducted in 2006 to investigate bioavailability of cadmium (Cd) and zinc (Zn) using 5 levels of salt treatments. It was a greenhouse study using maize (*Zea mays* L.) as indicator crop in a Completely Randomized Design (CRD). Soil data were analyzed using analysis of variance (ANOVA) in a SAS Computer package. Results showed that high rates of salinity decreased total Zn (Zn_T) and decreased Zn content of maize shoots. Application of $ZnSO_4$ decreased Cd in uptake shoots of maize (*Zea mays* L.) and increased shoot dry matter weight and yield. [Life Science Journal. 2007; 4(2): 64 – 68] (ISSN: 1097 – 8135).

Keywords: bioaccessibility; degradation; heavy metals; Kandiudult; remediation

1 Introduction

Zinc (Zn) is a micronutrient required for the maintenance of the integrity of biomembranes (Marschner, 1995). Obasi (2003) reported that application of Zn alone or in combination with copper (Cu) and iron (Fe) significantly reduced harvest drop and increased fruit weight, length, diameter and total yield of orange tree (*Citrus sinensis*). However, Zn complexes are formed under acidic pH range (Isirimah *et al*, 2003) and the element sorbs, thereby becoming unavailable when soils become alkaline (Tinker and Lauchi, 1984).

Cadmium (Cd) is a biotoxic heavy metal regarded as an important environmental pollutant in agricultural soils. Because of the potential adverse effects, it may pose to food quality, soil health and the environment (Gray *et al*, 2004). But it is the labile fraction rather than the total Cd content that is critical when assessing Cd availability in soils, and consequent bioacessibility in other forms of life.

Zinc and Cd are chemically similar as shown in chemical and physiological processes they undergo in soils andplants (Jalil *et al*, 1994). The bioavailability of cadmium element depends on the concentration form of the metal, concentration of Zn, soil pH, organic matter content, clay content, presence of other cations, complexing ligands and fertilization practices (Norvel *et al*, 2000).

In the humid tropics and indeed developing countries, scanty studies have been conducted on the above enumerated factors influencing biotoxic Cd. Onweremadu *et al* (2007) investigated the temporal variability of selected heavy metals in automobile soils and found that Cd concentrations in these soils are above critical limit. This study did not evaluate effects of these heavy metals on nutrient uptake.

Amidst limited attention given to Zn-fertilization (Takkar and Walker, 1993), it becomes necessary to investigate the effects of sanization in the uptake of Zn in cadmium polluted arable soils. The aim of this study was to assess the phytoavailability of cadmium and zinc when varying rates of sodium chloride (NaCl) were added in soils using maize (*Zea mays* L.) as an indicator crop.

2 Materials and Methods

2.1 Study area

The study was conducted at the University Teaching and Research Farm of Federal University of Technology, Owerri, Nigeria. The site is located on latitude 5º

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27′ 50″.230 N and longitude 7º 2′ 49″.330 E, with an elevation of 55 metres above mean sea level (Handheld Global Positioning System-GPS) receiver (Garmin Ltd, Kansas, United States of America). Soils are derived from Coastal Plain Sands (Benin formation). In an earlier study (Onweremadu *et al*, 2006) soils were classified as Isohyperthermic Arenic Kandiudult (Soil Survey Staff, 2003). The study area has over 2,500 mm of total annual rainfall. Temperatures are high and change only slightly during the year (mean daily temperature is about 27ºC). Rainforest vegetation predominates, although anthropogenic activities, especially urbanization, deforestation and farming have altered the original biodiversity.

2.2 Soil sampling

Surface soil samples were collected from cadmium-contaminated arable soil proximal to an automobile service station in 2006. Soils were classified as Isohyperthermic Arenic Kandiudult. Cadmium accumulation in the soils of the area is attributed to automobile wastes and inorganic fertilizer applications.

2.3 Greenhouse experiment

Bulk soil sample weighing about 300 kg was air-dried, crushed, thoroughly mixed and sieved to remove particle sizes greater than 2 mm. Sieved sample were brought to the greenhouse. Uniform soil weighing 3.0 kg was put into polyethylene pots (28 cm height, 19 cm diameter). 5-cm layer of well-washed sand was first filled in the pots to enhance drainage. Two levels of Zn (0 and 15 mg Zn/Kg dry soil, in the form of zinc sulphate) and 5 salinity levels were achieved using irrigation water with salinities of 0, 50, 100 and 150 mM NaCl, and 100 mM $NaNO_3$, respectively. An inclusion of $NaNO_3$ (sodium nitrate) helped to distinguish between effects of osmotic stress and chloro-cadmium complexation in solution on plant uptake. At planting, uniform rates of nitrogen and potassium fertilizers, 100 mg/kg N and K each ammonium sulphate and potassium sulphate respectively were applied to each pot. The fertilizer application was as recommended by The Fertilizer Procurement and Distribution Division (Federal Ministry of Agriculture and Natural Resources, 1990). These fertilizers were mixed thoroughly with soil before planting. Soil moisture content was maintained at field capacity (20%) gravimetric water using deionized water.

Maize seeds were sown and thinned to 2 plants per pot after 7 days of planting. Planting of maize was done in a Completely Randomized Design (CRD) with factorially arranged treatments and three replications. At harvest, shoots were cut at the soil surface, washed and dried at 70ºC.

2.4 Laboratory analysis

2.4.1 Soil samples: Particle size distribution was determined by hydrometer method (Gee and Or, 2002). Soil pH was estimated using a pH meter (Model 691 Metrohm AG Herisau, Switzerland) in a 1.2 soil/water ratio, while electrical conductivity in soil saturation extracts was determined with an FC-meter (Model Ohm-644 Metrohm AG, Herisau, Switzerland). Available phosphorus was extracted from the soil with 0.5 M $NaHCO_3$ and determined according to the procedure of Olsen and Sommers (1990). Available potassium was extracted with ammonium acetate and estimated using flame-photometer (Chapman and Pratt, 1961).

Total Cd and Zn contents were measured by microwave digestion using method 3051 (USEPA, 1995). In this method 0.5 g of air-dried subsample (less than 150 μm) was digested in XP1500 plus Teflon-PFA microwave vessel (CEM Corp, Mattews NC) using 9 ml of nitric acid and 3 ml of hydrochloric acid then filtered through Whatman No. 42 filters. This was transferred to 50 ml volumetric flasks and diluted with deionized distilled water (DDW). Chelate-extractable Cd and Zn were extracted using 0.005 M DTPA-TEA (Lindsay and Norvele, 1978) and then measured on a graphite furnace atomic absorption spectrophometer (GFAAS) (Perkin-Elmer 3400, Perkin Elmer Wellsely, MA).

2.4.2 Pant samples: The dried shoot materials were ground and ashed at a temperature of 550ºC for 7 hours and the ash was dissolved in hydrochloric acid. The digest solutions were used in the determination of Cd and Zn by GFAAS.

2.4.3 Post-harvest soil tests: After harvesting the maize, a sample of 800 g soil was collected from the soil surface of each pot, air-dried, crushed and sieved using a 2-mm sieve. Each soil sample was saturated with deionized water, mixed to a paste of uniform consistency and kept for 24 hours. After this, it was transferred to the suction flask for extraction of the soil solution. Soil pH and EC of the saturated extract, concentrations of Ca, Mg, Na, K, SO_4^{2-}, HCO_3^-, P, NO_3^-, Cd, Zn and Fe were determined using the methods earlier described.

2.4.4 Data analysis: Soil and plant data were analyzed by analysis of variance using the SAS Computer programme (Little *et al*, 1996).

3 Results

3.1 Soil properties

Results of soil properties are shown in Table 1, indicating a sandy loam texture. Soil pH was extremely low.

Salinity level did not significantly ($P < 0.05$) affect soil pH (Table 2). Sodium cation concentration increased almost proportiorially to the applied sodium chloride and sodium nitrate (Table 2). This trend was followed by chloride anions. Results also showed that Cd concentrations in soil solutions increase significantly ($P < 0.05$) as sodium chloride rate increased (Table 2), and this statement is true for both experiments (that is, without Zn and with Zn treatment). Sodium nitrate application resulted to little rise in Cd concentration of saturated extract. Treatment with zinc sulphate ($ZnSO_4$) had little or no effect on dissolved Zn, whereas there was outstanding increase in sulphate anion concentration, resulting from the application of Zn to the soil system (Table 2).

3.2 Effects of salinization and zinc application on metallic concentrations in the maize shoot

Concentrations of Cd and Zn in maize shoots resulting from the treatments are presented on Table 3. Zinc treatment lowered Cd concentration in the shoot while it did not in the without Zn treatment. Again, increasing NaCl concentration significantly ($P < 0.05$) led to a rise in Cd concentrations in shoots in both zinc treatments (that is, without Zn and with Zn treatments). On the other hand, application of sodium nitrate had no significant effect on Cd concentrations in shoots of maize.

Table 1. Selected soil properties of the surface soil sample (0 – 30 cm) used in the greenhouse study

Soil property	Value
Total sand	800.0 g/kg
Silt	40.0 g/kg
Clay	160.0 g/kg
pH_{water}	40.0
EC	2.1 mmhos/cm
Available P	15.4 g/kg
Available K	160.0 g/kg
DTPA-TEA extractable Zn	0.9 g/kg
DTPA-TEA extractable Cd	1.3 g/kg
Total Zn	26.4 g/kg
Total Cd	14.9 g/kg

Salinization decreased Zn content in shoots while $NaNO_3$ treatment had little or no effect on zinc concentration in shoots (Table 3). However, Zn content increased in maize plants receiving $ZnSO_4$ when compared with those that did not.

Maize dry matter weight decreased significantly ($P < 0.05$) with increasing rate of NaCl application. Zinc application increased dry matter weight when compared without Zn treatment irrespective of salinity level (Table 4).

Table 2. Values of total ions in the saturated paste soil solution

	Concentration									
Salinity level	Ca^{2+} (mM)	Mg^{2+} (mM)	K^+ (mM)	Na^+ (mM)	HCO_3^- (mM)	Cl^- (mM)	SO_4^{2-} (mM)	Cd_T (mg/L)	Zn_T (mg/L)	pH (water)
Without Zn treatment										
0 NaCl	23	3.8	0.4	8	1.3	12	12	0.02	0.14	4.0
50 NaCl	24	4.3	0.6	18	1.3	27	13	0.02	0.11	4.1
100 NaCl	25	4.8	0.9	30	1.8	42	14	0.11	0.14	4.0
150 NaCl	25	4.8	1.3	46	2.3	58	16	0.41	0.12	4.0
100 $NaNO_3$	25	4.8	0.9	33	1.9	13	22	0.03	0.13	4.2
With Zn treatment										
0 NaCl	22	4.9	1.3	11	1.1	17	12	0.01	0.15	4.0
50 NaCl	23	4.9	0.8	20	1.2	29	17	0.04	0.13	4.0
100 NaCl	24	4.9	0.8	28	1.8	32	22	0.12	0.16	4.1
150 NaCl	24	5.0	1.8	33	1.9	56	21	0.41	0.16	4.0
100 $NaNO_3$	23	5.6	0.8	28	1.8	22	27	0.04	0.16	4.0
$LSD_{salinity\ (0.05)}$	2.7	0.3	0.2	1.8	0.1	2.2	3.1	0.20	0.03	NS
$LSD_{Zn\ (0.05)}$	1.6	0.2	0.1	1.1	0.1	1.3	2.0	0.01	0.03	NS

NS = Not significant, Cd_T = total Cd in the paste, Zn_T = total Zn in the paste

Table 3. Concentrations of Cd and Zn in maize shoots at different salt rates

Treatment	Salinity level (mM)	Cd (mg/kg)	Zn (mg/kg)
Without Zn treatment	0 NaCl	24.6	1.0
	50 NaCl	22.6	1.1
	100 NaCl	21.5	1.3
	150 NaCl	16.3	2.9
	100 $NaNO_3$	24.8	1.2
With Zn treatment	0 NaCl	56.5	0.1
	50 NaCl	48.0	1.0
	100 NaCl	36.9	1.0
	150 NaCl	39.0	2.2
	100 $NaNO_3$	49.8	0.2

$LSD_{salinity\ (0.05)}$: Cd, 0.3, Zn, 0.1; $LSD_{Zn\ (0.05)}$: Cd, 0.2, Zn, 0.1.

Table 4. Shoot dry weight of maize in relation of salinity level

Treatment	Salinity level (mM)	Shoot weight (g/plant)
Without Zn treatment	0 NaCl	14.8^{a}
	50 NaCl	14.3^{ab}
	100 NaCl	11.4^{bc}
	150 NaCl	7.8^{c}
	100 $NaNO_3$	12.6^{d}
With Zn treatment	0 NaCl	22.1^{a}
	50 NaCl	19.6^{ab}
	100 NaCl	16.2^{bc}
	150 NaCl	12.3^{c}
	100 $NaNO_3$	13.5^{c}

Means in the same column followed by the same letter(s) are not significantly different for each treatment.

4 Discussion

The total Cd content (Table 1) was very much above critical limits of 10 mg/kg (EPA/ROC, 1989), and 0.2 mg/kg (Roberts *et al*, 1994). The high sand content did not promote poor retentivity or there was very severe pollution of soils of the site by Cd, thus high values of Cd in the sites. Low pH values suggest complexation of Zn and its unavailability and this is in line with the findings of Foth (1984) that most essential nutrients become available at slightly acidic and neutral pH ranges (pH = 6.0 – 6.2) since these are of low base status soils. Because, the studied soils are not saline, high uptake of Cd is not suspected if crop are grown in the field. Yet treatment of soils at 5 salinity levels did not significantly ($P < 0.05$) alter soil pH.

Application of sodium chloride on maize through irrigation water added sodium cations which competed with other cations, such as hydrogen and aluminium cations for sorption in the exchange sites. Also addition of chloride anions may have attracted positively charged Cd ions to form Cd-complexes. These complexes may reduce Cd in soil solution available for maize uptake. Whereas $NaNO_3$ treatment did not increase Cd concentration in soil solution, higher salinity levels did.

Without zinc treatment, salinity influenced K ions in the saturated paste soil solutions (Table 2), indicating that cation exchange effect resulted from salinizing the irrigation water used in the experiment. The implication is that salinity levels altered not only K but other cations although in a negligible manner.

Salinized irrigation water significantly ($P < 0.05$) increased Cd content in the shoots of maize (*Zea mays* L.) as indicated in Table 3. It can be argued that this increase in shoot content of Cd is attributable to osmosis, but 120 mM sodium nitrate treatment had no significant effect on Cd plant concentrations in an experiment conducted by Smolders *et al* (1998).

There was a proportrionate decline in maize dry matter weight and yield resulting from salt applications (Table 4). This condition requires an application of zinc fertilizer to augment for deficiencies created by salinization. Such Zn fertilizers reduce plant uptake of boron, sodium and chlorine, and the associated low yield of maize.

The level of Cd in soil and maize shoots suggested chemical immobilization methods which rapidly increase exchange sites for Cd-adsorption (Chen, 1997). Applications of zeolite reduces the concentration of Cd that dissolves in polluted soils (Mench *et al*, 1994) while heavy applications of phosphates to concentrated soils can reduce Zn dissolved in soil solution by precipitation (Saeed and Fox 1979).

5 Conclusions

Salinization enhanced the mobilization of Cd in soils and this promoted bioavailability. As a consequence, there was increased Cd in maize shoots. The study also revealed that fertilization of soils with zinc decreased Cd concentrations in shoots of maize.

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