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Modelling of Heavy Metals Concentration in Maize (*Zea may L.*) Grown in Artificially Contaminated Soil

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Authors' contributions

The authors worked in collaboration to produce this article. Author ISE designed protocols for the study and monitored strictly all the stages involved. Author AAA performed the field experiment, carried out the laboratory analysis and wrote the first draft of the manuscript. Author TA derived the model equation and scrutinized MATLAB program used to generate model constants. Author RAW read through the entire manuscript for appropriate modification and improvement. The four authors read and approved the final manuscript.

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ABSTRACT

The response of maize (*Zea may L.*) to heavy metals (Cd, Cr, Cu, Pb and Zn) contamination was investigated in field experiments to predict the potential of the plant to extract metal toxicants. Experimental field was amended with increasing loads (2–10 kgha^{-1}) of either metal salts and/or metal- cow manure blend (metal/cow manure ratio 1:10. Maize plants were grown and monitored for changes in growth rate. Maize plant tissue metal concentrations were determined using standard method. Physicochemical parameters of the parent soil (control) determined were 6.20, 8.93%, 6.81 meq100^{-1}g, 0.54% and 87.50 mgkg^{-1} for soil pH, soil organic matter (OM), cation exchange capacity (CEC), total nitrogen and phosphorus respectively. Soil particle size analysis showed the predominance of the sand component (74.20%), followed by clay (23.70%) and the silt (2.10%). Pseudototal metal content (mgkg^{-1}) were 4.35, 3.00, 6.25, 0.50 and 14.25 for Cd, Cr, Cu, Pb and Zn

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respectively. The low levels of these metals in the parent soil suggested the need for spiking in order to assess and predict plant tissue metal concentration in the contaminated soil. The plants were generally greenish with linear growth attributes proportional to metal doses, suggesting some level of forbearance. The range of maize tissue metal concentration for Cd, Cr, Cu, Pb and Zn were 3.50 – 42.80, 3.40 – 21.80, 7.80 – 48.10, 2.50 – 30.40 and 10.20 – 44.75 respectively. Cu was most extracted from the plant while Cr was the least. Predictive models for plant tissue metal concentration were derived from soil pH, OM, plant available and pseudo-total metal with a close range of values. The models predicted the metal concentration in maize plant very well and the relationship is significant ($0.01 \leq p \leq 0.05$). However, extrapolation of the present experimental results and its broader application to other plants, still need further investigation.

Keywords: Modelling; heavy metal; concentration; cow manure and amendment.

1. INTRODUCTION

Whenever plants grow on contaminated soil, contaminants may be incorporated within the above ground tissue of the plants. Soils are contaminated with a heavy metal such as Pb, Cd, Cr, As, Cu, Zn, B, Co, Mo, Mn etc, many of which are non-essential and overtime toxic to plants, animals and human beings. This causes an undesirable change in the physical, chemical and biological characteristics of soil and affects human life, lives of animals and plants [1]. The uptake of heavy metals from soil by plants has received much attention in recent time because such studies are useful in the assessment of heavy metal contamination of soil and the prediction of adverse effects of plant growth, crop quality and ecotoxicity and human health [2].

Aside from the natural sources, most other possible sources of toxic metals in contaminated and growth Media are traceable to uncontrolled human activities from the agricultural input, energy production, mining and smelting, secondary metal production and recycling operations, urban-industrial complexes and automobile emissions [3,4]. Migration of metals in the soil is influenced by physical and chemical characteristics of each specific metal and by several environmental factors. The most significant environmental factors appear to be soil type, total organic content, redox potential, and pH [5]. Although heavy metals are generally considered to be relatively immobile in most soils, their mobility in certain contaminated soils may exceed ordinary rates and pose a significant threat to soil organisms and water quality [6].

Monitoring the concentration of heavy metals in soil is of interest due to their influence on the ground- and surface- water, flora, animals and humans [7]. Heavy metals such as Cd, Cu, Pb, Hg and Ni in excessive amount have found to be potentially carcinogenic, mutagenic as well as teratogenic. Heavy metals like some other pollutants on acute or chronic exposure severely affect different body organs [8]. Children exposed to lead are at the risk for impaired development, lower IQ, shortened attention span, hyperactivity and mental deterioration, with children under the age of six being at a more substantial risk. Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia and weakness of the joints when exposed to lead [9]. Metal mobility is closely related to metal solubility, which is further regulated by adsorption, precipitation and ion exchange reaction in soils [10,11]. Heavy metal accumulation in soil, water and crops, and their health impact on residents is a persistent social issue in many countries, Nigeria inclusive [12, 13]. Heavy metal solubility and mobility in soils are of environmental significance due to their potential toxicity to both animals and plants [14]. Soil pollution of these chemical substances enhances plant uptake causing accumulation in plant tissues and eventually phytotoxicity and change of plant community [15].

The assessment of risks and responses of common crop plants to soil metal is essential in order to detect and identify the occurrence of metal toxicity so as to ensure food quality and effectively regulate metal emissions to the environment [16]. Plants are good indicators of the health of the soil on which they are growing. The aerial parts of all plants are a collector for all soil and air pollutants and their chemical composition may be a good indicator for contaminated areas when assessed against background values obtained for unpolluted vegetation. High metal accumulating ability has been reported for cereals crops [17], an attribute that can be used as an indicator of the level of soil contamination and in the passive monitoring of the environment [18]. Maize (*Zea mays L.*) is one of the most popular cereal crops that is widely cultivated throughout the world in different agroecological environments. The crop is a potential heavy metal accumulator: it has high biomass production, extensive fibrous root system, high soil-plant transfer coefficient, fast growing and heavy metal tolerant [19].

Contaminated agricultural soils or disturbed soils exhibit a variety of problems that often can be addressed effectively and directly through the use of soil amendments. These problems include the toxicity of various soil contaminants, a higher- or lower-than-normal soil pH, excess Na limit plant rooting and water and nutrient uptake, and can cause toxicity to plants [20]. The most widespread visual evidence of heavy metal toxicity is a reduction in plant growth [21] including leaf chlorosis, necrosis, turgor loss, a decrease in the rate of seed germination, and a crippled photosynthetic apparatus, often correlated with progressing senescence processes or with plant death [22]. Angelova et al. [23] investigated the impact of organic amendments on the uptake of heavy metals (Pb, Zn, Cd, and Cu) by potato *(Solanum tuberosum L.)* plants. They found a correlation between the quantity of the mobile forms and the uptake of metals by potato and reported decreased heavy metal content in potato peel and tubers due to successful immobilization of Pb, Cu, Zn, and Cd by organic amendments. Addition of compost or manure together with lime to raise soil pH is a common practice for immobilization of heavy metals and soil amelioration, to facilitate re-vegetation of contaminated soils [24]. A chelating agent such as EDTA can mobilize soil metals and increase their bioavailability to the plants [25].

Most of the recent investigations deal with the plants are grown in a heavy metal contaminated soil and analysed experimentally to determine their ability to remove them. Complete knowledge concerning predictive models based on soil-to-plant heavy metal interaction derived from experimental data is still lacking.

Soil-plant related properties can be expressed with multivariate regression equations:

$$\log{[M]_p} = Q\log{[M]_S} + \delta \quad (1)$$

Where $[M]_S$ is the plant available metal in soil solution determined by extracting with 0.01 M Calcium chloride solution and $[M]_P$ is a metal concentration in plant [26]. It is possible to forecast $[M]_P$ from soil parameters such as pH, soil organic matter etc because there is a close relationship among soil properties, the metal content in the soil and the concentration in the soil solution [27]:

$$\log{[M]_S} = Q_2\log{[M]_T} + \beta_1 pH + \gamma logOM + \delta_1 \quad (2)$$

Where $[M]_T$ is the pseudototal metal content in the soil. Combination of equations (1) and (2) can be used to predict metal concentration in maize tissue from soil parameters without necessarily measure the soil solution [28,29].

$$\log{[M]_P} = Q_3\log{[M]_T} + \beta_2 pH + \gamma_2 logOM + \delta_2 \quad (3)$$

The values of the model coefficients $Q,\ \beta,\ \gamma\ and\ \delta$ would be different for each of the model equation.

There are combinations of factors affecting metal uptake by plants. Multivariate regression method is applied to find dominant factor influencing metal uptake by the plant when considered stepwise [30].

Careful experimentation using novel devices, in tandem with comprehensive modelling will lead to better understanding of what controls the bioavailability, uptake, transport, and fate of chemical elements in the soil [31].

2. MATERIALS AND METHODS

2.1 Chemical and Apparatus

Some of the chemicals used were: lead nitrate (99.0 % w/w), chromium (II) nitrate nonahydrate (99.0% w/w), copper (II) nitrate trihydrate (99.0% w/w), cadmium nitrate tetrahydrate (99.0% w/w), zinc nitrate hexahydrate (99.0% w/w) , hydrogen peroxide (30% w/v), hydrochloric acid (37% w/v), nitric acid (99.5% w/v) calcium chloride, ethy lenediaminetetraacetic acid, EDTA (99.0% w/w). All chemicals used were Fluka and Riedel-de Haën products marketed by Sigma-Aldrich, Buchs, Switzerland. Apparatus used include normal laboratory glassware (borosilicate), polyethylene vessels, pH meter (Jenway, 3510), Atomic Absorption Spectrophotometer (Buck Scientific VGP 210).

2.2 Study Site

This study was carried out on an agricultural research farm in Kogi State University (KSU), Anyigba (7^0 36' N 7^0 12' E), Eastern part of Kogi

State, North Central, Nigeria. The climate of the region is characterized by two seasons: dry and wet. The rainy season occurs between April through October and the peak in September with about four months of dry seasons. Relative Humidity generally rises to over 80% in the morning and falls between 50%-70% in the afternoon during the wet season. Heavy rains of conventional type are common in the area and this sometimes amounts up to about 978.5 mm but maybe more. The average rain days for the area were approximately 74.0 days. The mean monthly temperature ranges between 21°C and 32°C. The highest temperature occurs just before the rainy season begins [32].

2.3 Soil Sampling and Characterization

Soil samples were collected with a soil auger at different locations on the experimental field before and after amendments. The soil samples collected were air dried, pounded using a mortar and pestle and sieved through 2 mm mesh to remove stones and other plant materials [33]. These were then packaged in polythene bags as parent soil (control). Both parent soil (PS) and cow manure were characterized in terms of pH [34], textural analysis [35], organic matter content (OM) [36], Cation exchange capacity, CEC [37], plant available phosphorus [38] and soil total nitrogen [39]. Soil total Pb, Cd, Cr, Cu and Zn contents were determined by the method described by Uwumarongie and Okieimen, [29]: exactly 5 mL of aqua regia and 1 mL of perchloric acid were added to 1.0 g of soil sample in a 150 mL digestion tubes and heated until a clear digest appeared. The tube was cooled and the side rinsed with distilled-deionized water and then filtered through a Whatman No.1 filter paper into a 100 mL volumetric flask. The volume was made up with distilled-deionized water. The concentration of the heavy metals in the extract was determined in a pre-calibrated Atomic Absorption Spectrophotometer.

2.4 Experimental Field Design and Soil Amendment

The experimental field was plowed and ridged mechanically and split into three (3) main plots. Plot one (1) was used for control experiment (unamended soil). Each of plot two (2) and three (3) was divided into four (4) subplots to generate a total of eight (8) subplots. Each subplot was contaminated with increased doses of soluble metal salts either singly or a binary mixture of metal salt with cow manure in the ratio of 1:10. The metal doses were 0 (control), 2, 4, 6, 8 and 10 $kgha^{-1}$. The amended soil was allowed to stabilize for one month before planting operation. These implied that the five metals were applied either singly or co-jointly with cow manure to simulate soil contamination by heavy metals from various anthropogenic sources under the influence of organic and inorganic amendments. The soil treatments were designated as either soil- metal or Soil-metal- cow manure plot respectively. The added metals were listed among common soil contaminants [40]. The amended soils were similarly characterized physicochemically in terms of pH, particle size, organic matter content, cation exchange capacity and soil total metal contents.

2.5 Planting of the Maize

The seeds of improved variety (SUWAN-1-SR) maize were obtained from Kogi State Agriculture Development Project (KADP) Lokoja and planted on 5th May 2016. Five seeds of maize were planted at an interval of 60 cm and the seedlings thinned to three after germination to keep the strongest plantlets per stand. The plant was monitored for 90 days for changes in height, colour and tissue metals (Pb, Cd, Cr, Zn and Cu) concentrations. The above ground plant biomass (leaves and straw) were harvested from the soils after 90 days of cultivation.

2.6 Assay of Plant Available Metals and Digest of Plant Biomass

Chemical extraction of soil with 0.01 M calcium chloride solution was used to determine plant available metals [26]. Leaves and straws of the maize plant were harvested on 3rd August 2016 according to the experimental design (after 90 days of cultivation). They were rinsed with distilled- deionized water to remove adhered soil, air dried under laboratory condition and pounded into powder with a mortar and pestle. Exactly 1.0 g powdered plant sample was digested with a mixture of 4.0 mL of 65% nitric acid and 2.0 mL of 30% hydrogen peroxide. The mixtures were heated and evaporate to almost dryness. Then, 4.0 mL of concentrated nitric acid and 2.0 mL of concentrated hydrogen peroxide was added to the residue and heated until a clear digest appeared. The total digestion time was 4h at 120 ^{o}C. It was then set aside to cool and filtered into 20 mL volumetric flask. It was made up to mark with distilled- deionized water (DDW). The concentration of Cd, Cr, Cu, Pb and Zn ($mgkg^{-1}$dry weight of plant sample) was determined from the digest using Atomic Absorption Spectrophotometer (Buck Scientific VGP 210) at the wavelength of 228.80, 357.90, 324.75, 283.31 and 213.86 nm respectively [41].

2.7 Quality Control and Statistical Analysis

All glassware and plastics used were soaked in dilute nitric acid overnight and washed with Teepol and rinsed with distilled-deionized water. Blank determinations were carried out by subjecting the same amount of reagents to similar procedures to check reagent's impurities and other possible environmental contaminations during analysis. Validations of analytical methods included the use of standard reference materials were available and analysis by different models of analytical instruments. The statistical analysis was performed on triplicate results of each sample. The mean and standard deviation of each value was calculated using 2-way analysis of variance (ANOVA) to compare the differences in mean values across the various sample locations, treatment and control samples investigated. MATLAB (7.10.0499, R2010a) statistical software was used to generate constant components in stepwise multivariate regression models to predict maize tissue metal concentrations from soil parameters such as pH, organic matter, plant – available and pseudo total metals with the assumption that they are a covariate. The significance of model parameters was set at ($0.01 \le P \le 0.05$).

3. RESULTS AND DISCUSSION

The properties and functions of soil in relation to biota depend on its physical and chemical factors. Some physicochemical parameters of the soil were evaluated and they include pH, soil organic matter (OM), cation exchange capacity (CEC), soil texture and pseudo-total metal. The pH value of parent soil (unamended) was 6.20 whereas that of the raw cow manure was 6.50. The weak acidic pH value of 6.20 recorded for the parent soil is within the limit of agronomic practices [42]. Soil organic matter, the sum total of all carbon-containing substances in the soil was determined to be 8.93% for the parent soil and 40.60 for the raw cow manure respectively. The organic matter content of this soil qualifies it as a mineral soil, a property that favour plant growth on most agricultural soil.

Cation exchange capacity (CEC) is the sum total of exchangeable cations between the soil surface and aqueous solution. Cation exchange capacity of the parent soil was 6.81 meq/100 g. Generally, soil organic matter and clay content are responsible for the bulk of soil CEC [43]. The lower CEC observed in the parent soil can be related to their sandy nature and low organic matter content. Particle size (textural) analysis showed the predominance of the sand component (74.20%), followed by clay (23.70%) and then silt (2.10%).Thus, it portrayed the parent soil as sandy. Sandy soils are known to have a low retention capacity for both water and heavy metal ions. It can, therefore, be forecasted that given relative sufficient period of time and other suitable environmental conditions such as pH, absorbed heavy metals can be easily mobilized and leached to lower soil layers, thereby adversely affecting nearby underground water resources. The pseudo-total Cd, Cr, Cu, Pb and Zn concentrations ($mgkg^{-1}$) in the parent soil were 4.35, 3.00, 6.25, 0.50 and 14.25 respectively. Whereas their concentrations ($mgkg^{-1}$) in the cow manure were 0.30, 2.20, 17.50 and 23.10 for Cd, Cr, Cu, and Zn respectively. The lead was not detected in the cow manure probably due to the animal's mode of feeding. Low level of heavy metals in the parent soil implied that the control soil was comparatively uncontaminated, hence the need for amendments in order to assess and predict heavy metal concentration in maize (*Zea may L.)* in a contaminated soil.

3.1 Growth Attribute of Maize Plant in Response to Contaminants

The most common visual evidence of plants response to a heavy metal contaminant is its growth properties and biomass. Maize plants were monitored periodically (weekly) for changes in height within the time span of 1-12 weeks. The results are shown in Figs. 1 and 2. In the soil-metal salt treatment, growth curves of maize appeared to be sigmoid (S in shape); that is plant height increased slowly in the first three weeks, followed by a rapid increased up to the eighth week and then followed by slower and constant height by the tenth week. Changes in height with time were statistically significant ($0.01 \le P \le 0.05$) for all the treatments. Generally, growth rates were faster at lower dose and slowed down with increasing metal load in the soil. In the soil-metal- cow manure stressed soil; maximum maize height was 172 cm, (Fig. 2), 156 cm for soil- metal (Fig. 1). Overall, the soil- metal cow manure scenario recorded the greatest heights.

Growth response of maize to metal studied followed the order: Cu > Zn > Pb > Cd > Cr. This suggested that maize was most tolerant to Cu than other metals studied. Copper is one of the essential elements required by plants. Generally, the separation between individual growth curves seemed to be more distinct in Cu and Zn than other metals.

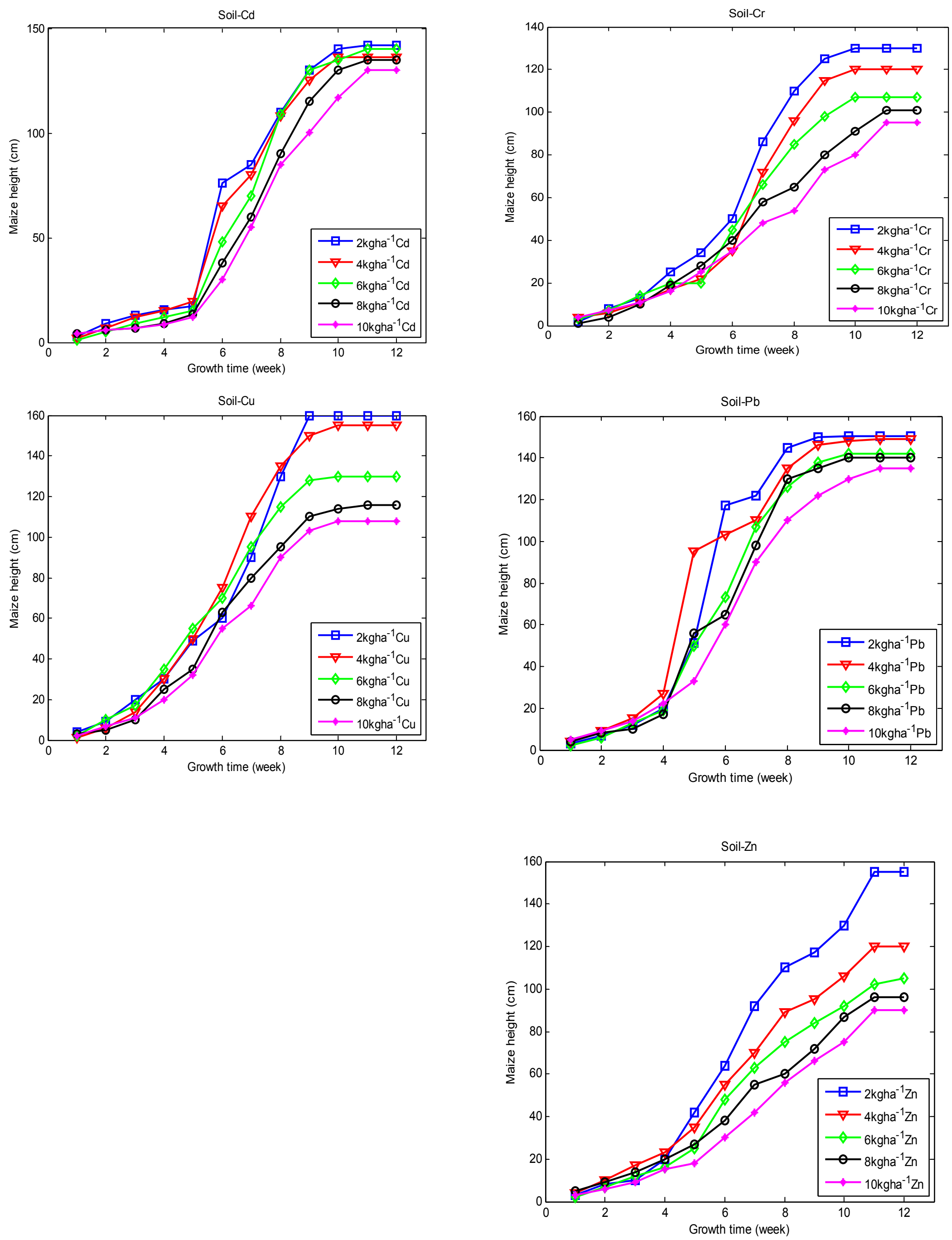

Fig. 1. Growth profiles of maize plant in soil contaminated with different doses of metals

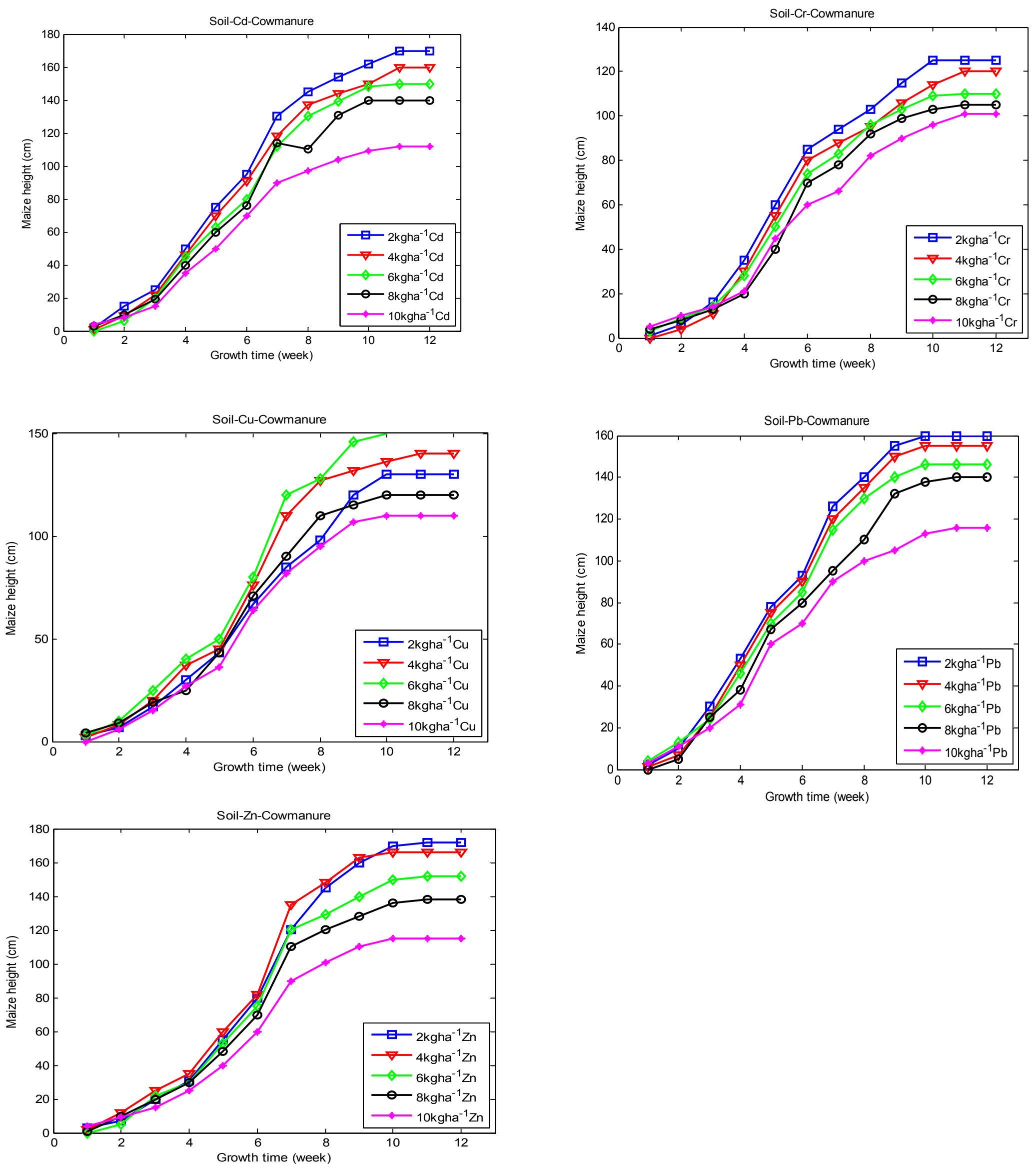

Fig. 2. Growth profiles of maize plant in soils contaminated with different doses of metal blended with cow manure. Metal/Cow manure ratio 1: 10

The results of metal concentration in maize grown in soil contaminated with only metal salts are shown in Table 2. From the Table, it was observed that metal concentration in maize plant increased with loading rate in the soil. The ranges of heavy metal level in the plant tissue based on dry weight (dw) were 8.25 – 35.20 mgCdkg^{-1}, 7.80 – 17.10 mgCrkg^{-1}, 19.20 – 43.50 mgCukg^{-1} 6.50 – 25.20 mgPbkg^{-1}, and 17.30 – 40.70 mgZnkg^{-1}. The absorption of heavy metals by plants depends on their concentration in the soil, soil pH, species and variety of plant among other factors [44,45]. High heavy metal accumulating ability has been reported for cereals crops such as sorghum and alfalfa [46]. Plants can tolerate high levels of metals in their environment using either the exclusion mechanism, by which the plant maintain metal concentration in the shoots at constant or low levels and occurs when the entrance of metals into the roots of the plants are restricted or translocation of metals from the roots to the shoots of the plants are restricted [46] or by accumulation mechanism by which metals are concentrated in plant parts [47].

Table 1. Some physicochemical parameters and total heavy metal concentrations of parent soil (Control) and raw cow manure

Parameters	Unamended Soil	Cow manure
$pH_{(S)}$	6.20 ± 0.10	6.50 ± 0.21
Organic Matter (%)	8.93 ±0.60	40.60 ± 0.30
Exchangeable:		
Na (meq/100 g)	0.18 ± 0.20	
K (meq/100 g)	4.66 ± 1.00	
Mg (meg/100 g)	0.72 ± 0.00	
Ca (meq/100 g)	1.25 ± 0.10	
CEC(meg/100 g)	6.81 ± 1.30	
Total Nitrogen (%)	0.54 ± 0.12	0.72 ± 0.20
Available P ($mgkg^{-1}$)	87.50 ± 2.10	91.20 ± 0.30
Clay (%)	23.70 ± 0.50	
Silt (%)	2.10 ± 0.30	
Sand (%)	74.20 ± 0.10	
Pseudototal Metal Content ($mgkg^{-1}$):		
Cd	4.35 ± 1.00	0.30 ± 0.50
Cr	3.00 ± 0.20	2.20 ± 0.00
Cu	6.25 ± 0.60	17.50 ± 2.00
Pb	0.50 ± 0.40	-
Zn	14.25 ± 0.00	23.10 ± 0.40

Note: Values are given as the mean of triplicate determinations ± standard deviation

Table 2. Concentration of heavy metal in maize tissue, $[M]_P$ ($mgkg^{-1}$ dw); plant available metal in the soil, $[M]_S$ ($mgkg^{-1}$); pseudototal soil metal, $[M]_T$ ($mgkg^{-1}$); soil pH and percentage organic matter (OM) of soil loaded directly with metal salts in the range of 2-10 $kgha^{-1}$

Metal	Dose ($kgha^{-1}$)	$[M]_P$	$[M]_T$	$[M]_S$	pH	OM
Cd	2	8.25 ± 0.70	68.25 ± 0.21	22.20 ± 0.10	6.20 ± 0.13	10.70 ± 0.10
	4	11.65 ± 0.40	85.00 ± 0.00	32.90 ± 0.00	6.80 ± 0.40	11.10 ± 0.22
	6	30.50 ± 0.21	136.50 ± 0.21	31.75 ± 0.40	6.50 ± 0.30	11.70 ± 0.31
	8	32.10 ± 0.31	179.75 ± 0.40	48.00 ± 0.22	7.20 ± 0.20	12.20 ± 0.11
	10	35.20 ± 0.15	220.00 ± 0.50	52.30 ± 0.13	7.40 ± 0.12	14.00 ± 0.10
Cr	2	7.80 ± 0.40	13.78 ± 0.31	9.50 ± 0.00	6.20 ± 0.14	10.80 ± 0.40
	4	9.00 ± 0.14	24.20 ± 0.30	13.60 ± 0.11	6.45 ± 0.50	11.20 ± 0.00
	6	9.30 ± 0.10	48.80 ± 0.00	15.25 ± 0.50	5.76 ± 0.31	15.50 ± 0.20
	8	12.80 ± 0.60	63.25 ± 0.70	26.50 ± 0.40	6.60 ± 0.22	17.60 ± 0.00
	10	17.10 ± 0.23	71.82 ± 0.50	28.60 ± 0.10	6.70 ± 0.11	20.11 ± 0.22
Cu	2	19.20 ± 0.21	48.20 ± 0.20	22.00 ± 0.11	5.80 ± 0.11	11.52 ± 0.40
	4	24.40 ± 0.11	51.60 ± 0.30	23.50 ± 0.40	6.02 ± 0.12	13.50 ± 0.13
	6	31.70 ± 0.50	139.80± 0.50	27.10 ± 0.21	6.40 ± 0.50	15.90 ± 0.20
	8	27.40 ± 0.41	211.12 ± 0.00	30.40 ± 0.13	6.70 ± 0.23	18.10 ± 0.22
	10	43.50 ± 0.21	287.18 ± 0.00	35.00 ± 0.21	6.80 ± 0.00	20.20 ± 0.22
Pb	2	6.50 ± 0.22	90.00 ± 0.30	19.80 ± 0.22	6.20 ± 0.12	10.00 ± 0.20
	4	10.60 ± 0.11	224.75 ± 0.00	20.65 ± 0.13	6.30 ± 0.14	10.50± 0.20
	6	17.30 ± 0.00	244.02 ± 0.11	25.55 ± 0.50	6.52 ± 0.70	11.20 ± 0.11
	8	23.45 ± 0.30	293.25 ± 0.10	37.10 ± 0.12	6.70 ± 0.11	12.00 ± 0.21
	10	25.20± 0.20	502.00 ± 0.11	40.50 ± 0.11	6.40 ± 0.21	11.80 ± 0.33
Zn	2	17.30 ± 0.33	133.75 ± 0.23	21.25 ± 0.00	6.50 ± 0.10	12.76 ± 0.14
	4	23.50 ± 0.14	140.70 ± 0.40	29.50 ± 0.14	6.60 ± 0.13	11.90 ± 0.12
	6	30.10 ± 0.11	170.00 ± 0.60	35.30 ± 0.11	6.80 ± 0.22	16.20 ± 0.30
	8	35.50 ± 0.30	236.25 ± 0.20	43.20 ± 0.60	7.50 ± 0.12	19. 50 ± 0.23
	10	40.70 ± 0.12	315.00 ± 0.00	47.60 ± 0.11	7.60 ± 0.00	22.50 ± 0.11

Note: Values are given as the mean of triplicate determinations ± standard deviation

By-products from organic matter decomposition in cow manure could also form complexes or chelates with heavy metals that may affect their bioavailability. Table 3 presented the results of heavy metal concentration in maize from metal cow manure treated soil. Harvestable tissue concentration of maize were 3.50-37.20 $mgCdkg^{-1}$, 4.50-14.40 $mgCrkg^{-1}$, 14.50-32.70 $mgCukg^{-1}$, 2.50-21.00 $mgPbkg^{-1}$ and 11.25 -31.60 $mgZnkg^{-1}$. Metal uptake by the plant under cow manure treated soil was low relative to only metal salt amended soil. The presence of organic matter in the cow manure might have provided protection against metal uptake by maize plant due to resistant to decomposition [48]. Cow manure may contain heavy metal sorbents such as Al, Mn, Fe oxides, organic matter capable of reducing heavy metal solubility, thereby stabilizing them in the soil [3]. The uptake of Cu by the plant was higher than that of Zn. Similarly, the amount of Cd measured in the aerial part of the plant was larger than that of Pb. These results confirmed with the earlier observation that Cd availability in the soil and hence its uptake by maize plant was more than that of Pb, which is consistent with the results reported by Alloway [49]: his report inferred that Cd has a tendency for being more mobile in soils and therefore more available for plants uptake than other metals, including Pb. Metal uptake somewhat decreased with increase in the applied those of cow manure. Many biosolids residual such as cow manure, sewage sludge, municipal solid waste, compost etc contained sufficient amounts of organic matter, phosphate and inorganic oxides and/or have favourable properties (e.g pH) that can reduce metal solubility and phytoavailability, [3]. The sorbent phase responsible for the reduction of metal bioavailability in biosolids has been a subject of much interest, while some workers suggest that heavy metals are sequestered by chelation with organic matter [48], others point to the inorganic surfaces in biosolids as the heavy metals binding centers [21,32].

Table 3. Heavy metal concentration ($mgkg^{-1}$ dw) in harvested maize tissue grown on soil amended with metal-cow manure blend. Metal/Cow manure ratio 1:10

Metal	Dose ($kgha^{-1}$)	$[M]_P$	$[M]_T$	$[M]_S$	pH	OM
Cd	2: 20	27.70 ± 0.20	63.65 ± 0.11	20.15 ± 0.00	6.30 ± 0.32	19.20 ± 0.22
	4: 40	31.60 ± 0.11	71.75 ± 0.40	26.50 ± 0.13	6.50 ± 0.11	20.80 ± 0.11
	6: 60	12.00 ± 0.00	82.17 ± 0.30	30.00 ± 0.21	6.40 ± 0.14	21.50 ± 0.30
	8: 80	3.50 ± 0.15	110.13 ± 0.60	41.60 ± 0.30	6.70 ± 0.12	31.50 ± 0.31
	10: 100	37.20 ± 0.13	168.85 ± 0.53	49.40 ± 0.14	6.80 ± 0.00	35.20 ± 0.21
Cr	2: 20	4.50 ± 0.10	20.13 ± 0.60	7.70 ± 0.13	6.00 ± 0.10	17.25 ± 0.00
	4: 40	6.18 ± 0.21	36.89 ± 0.00	9.20 ± 0.20	6.20 ± 0.20	18.80 ± 0.40
	6: 60	9.20 ± 0.11	50.15 ± 0.80	17.40 ± 0.00	6.50 ± 0.50	20.80 ± 0.42
	8: 80	11.50 ± 0.31	52.00 ± 0.30	17.90 ± 0.11	6.64 ± 0.00	28.20 ± 0.12
	10: 100	14.40 ± 0.12	57.00 ± 0.10	21.50 ± 0.21	5.90 ± 0.12	31.60 ± 0.11
Cu	2: 20	32.70 ± 0.11	98.00 ± 0.21	15.20 ± 0.11	6.20 ± 0.00	18.80 ± 0.31
	4: 40	21.40 ± 0.00	93.14 ± 0.50	18.00 ± 0.10	6.40 ± 0.11	20.40 ± 0.30
	6: 60	14.50 ± 0.11	107.40 ± 0.14	20.25 ± 0.30	6.50 ± 0.21	25.50 ± 0.14
	8: 80	21.60 ± 0.12	182.40 ± 0.90	22.30 ± 0.00	6.80 ± 0.15	27.50 ± 0.21
	10: 100	18.20 ± 0.41	260.35 ± 0.10	27.55 ± 0.10	7.30 ± 0.22	29.80 ± 0.11
Pb	2: 20	21.00 ± 0.30	90.45 ± 0.50	18.30 ± 0.10	6.10 ± 0.00	15.70 ± 0.70
	4: 40	14.25 ± 0.00	102.25 ± 0.70	21.00 ± 0.21	6.20 ± 0.11	18.10 ± 0.30
	6: 60	5.75 ± 0.23	223.23 ± 0.14	23.15 ± 0.11	6.50 ± 0.20	22.50 ± 0.22
	8: 80	4.10 ± 0.21	277.12 ± 0.20	30.60 ± 0.30	5.90 ± 0.10	27.60 ± 0.10
	10: 100	2.50 ± 0.10	321.25 ± 0.41	33.50 ± 0.00	6.60 ± 0.14	30.40 ± 0.60
Zn	2: 20	26.50 ± 0.13	83.00 ± 0.30	19.25 ± 0.40	6.30 ± 0.17	21.46 ± 0.22
	4: 40	15.50 ± 0.14	91.00 ± 0.20	24.60 ± 0.12	6.40 ± 0.11	22.50 ± 0.11
	6: 60	31.60 ± 0.30	100.00 ± 1.00	31.10 ± 0.11	6.40 ± 0.13	28.30 ± 0.20
	8: 80	20.30 ± 0.22	170.00 ± 0.50	37.20 ± 0.22	6.70 ± 0.00	30.60 ± 0.31
	10: 100	11.25 ± 0.50	303.75 ± 0.60	45.50 ± 0.60	6.80 ± 0.00	33.75 ± 0.21

Note: Values are given as the mean of triplicate determinations ± standard deviation . $[M]_P$, metal concentration in maize; $[M]_S$, plant available metals; $[M]_T$, pseudototal soil metal; pH , soil pH ; OM, soil organic matter

Table 4. Multivariate regression models relating concentration ($mgkg^{-1}$) of heavy metal in maize tissue to properties of soil when loaded singly with metal salts

Metal	Model equations	Model validation	
		R^2_S	R^2_{adj}
Cd	I. log $[M]_P$ = 1.61log$[M]_S$ – 1.19	0.83	0.80
	II. log $[M]_p$ = 6.12log$[M]_s$ – 1.57pH – 1.97logOM + 0.40	0.95	0.79
	III. log$[M]_P$ = 2.09log$[M]_T$ – 0.16pH – 2.43logOM + 0.62	0.91	0.90
Cr	I. log $[M]_P$ = 0.65log$[M]_S$ + 0.23	0.79	0.77
	II. log $[M]_p$ = -0.22log$[M]_S$ + 0.19pH + 1.20logOM – 1.29	0.93	0.91
	III. log$[M]_P$ = -0.05log$[M]_T$ + 0.15pH + 1.00logOM – 1.01	0.89	0.83
Cu	I. log $[M]_P$ = 1.46log$[M]_S$ – 0.65	0.90	0.87
	II. log $[M]_p$ = 0.81log$[M]_S$ – 0.84pH + 4.26logOM + 0.59	0.96	0.93
	III. log$[M]_P$ = 0.57log$[M]_T$ – 1.54pH + 6.00logOM + 3.00	0.87	0.85
Pb	I. log$[M]_P$ = 1.61log$[M]_S$ – 1.14	0.75	0.73
	II. log$[M]_P$ = -1.09log$[M]_S$ – 0.56pH -14.49logOM – 8.80	0.95	0.89
	III. log$[M]_P$ = 0.31log$[M]_T$ + 0.09pH + 4.71logOM – 5.07	0.92	0.90
Zn	I. log $[M]_P$ = 1.06log$[M]_S$ – 0.17	0.84	0.81
	II. log $[M]_p$ = 1.04log$[M]_S$ – 0.06pH + 0.30logOM - 0.07	0.97	0.93
	III. log$[M]_P$ = 0.33log$[M]_T$ + 0.85pH + 0.36logOM – 0.33	0.88	0.86

Note: All R^2 values are significant at $0.01 \le p \le 0.05$. $[M]_P$, metal concentration in maize; $[M]_S$, plant available metals; $[M]_T$, pseudototal soil metal; pH, soil pH; OM, soil organic matter

Table 4 presented model equations used to predict metal concentration in maize plant cultivated in metal salt amended the soil. The range of some soil physical and chemical properties used to generate constants component (Q, β, γ and δ) of the model equations were (5.76- 7.60) and (10.0- 22.50) for soil pH and percentage soil organic matter respectively. Others were (22.20- 52.30), (9.50- 28.60), (22.00- 35.00), (19.80- 40.50) and (21.25- 47.60) for Cd, Cr, Cu, Pb and Zn soil available metal, $[M]_S$ respectively (Table 4). Value for each constant indicated that individual contribution of a predictor variable to the model. For Cd in Table 4, value of 1.61 implied that the concentration of Cd in the maize plant would improve by 1.61 for a unit increment of Cd concentration in the soil. Conversely, β value of -1.57 (equation II) suggests that concentration of Cd in maize plant would decrease by -1.57 for a unit increase in soil pH when other variable remained constant.

The significance of the equation was tested by the coefficient of determination (R^2) and probability (p-value) [50]. R^2 values revealed that soil Cd, Cr, Cu, Pb and Zn contents explained the variability of the metal in maize to the rank of ≥ 75% and showed a significant relationship ($0.01 \le p \le 0.05$). R^2_{adj} was expected to be the same or as close to the value of R^2. However, in the case of Cd, they differed by 0.03, 0.16 and 0.01 for equations I, II and III, respectively. This shrinkage means that if the models were derived from the population rather than a sample, it would account for approximately 3%, 16% and 1% less variance in the outcome respectively.

4. CONCLUSIONS

The effect of increasing heavy metal levels and/or cow manure amendment on plant available metal, growth and phytoextraction ability of *Zea may L.* (maize) was investigated and modeled. Heavy metal mobilities were lower in the soil-metal-cow manure media than a metal amendment, an indication that cow manure can reduce solubility, mobility and environmental risk associated with heavy metal contaminants.

Multivariate regression models indicated plant available metal to be the most dominant factor influencing metal level in maize. High R^2 values for the model equations implied that they explained the dependent variable satisfactorily and the relationship is significant ($0.01 \le p \le 0.05$). The regression models may be used to predict metal concentration in maize plant from the heavy metal contaminated soil. However, an extension of the present experimental results and its broader application to other plants, still need further investigation.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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