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Immobilization Potential of Cow Manure for Heavy Metal Remediation from Refuse Dump Soil

Ezeudu Emeka Christian[1*], Oli Christian Chukwuemeka[1], Enenche[1], Elaigwu Daniel[1], Anekwe Ozioma Juliana[1], Okoye Patrice-Anthony Chudi[1] and Ajiwe Vincent Ishmael Egbulefu[1]

[1]Nnamdi Azikiwe University, Awka, Nigeria.

Authors' contributions

This work was carried out in collaboration among all authors. Authors EEC, OPAC and AVIE designed the study. Author EEC carried out the experiment. Authors OCC and AOJ wrote the protocol and the first draft of the manuscript, while authors E and ED managed the analyses of the study, the literature searches and performed the statistical analysis. All authors read and approved the final manuscript

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ABSTRACT

Aims: The present study investigated the effect of cow manure amendment on fractionation and availability of some heavy metals (Cd, Cu, Cr, Mn, Pb and Zn) in refuse dump soil.
Study Design: A greenhouse study experiment was conducted to determine the uptake of the metals by *Ricinus communis* in dump soil treated with 0%, 5%, 10% and 20% cow manure.
Place and Duration of Study: The study was carried out at the Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University Awka, Anambra State, Nigeria, between May and October 2018.
Methodology: Experimental pots were filled with 2.0kg refuse dump soil in a green house and treated with 5%, 10% and 20% of Cow manure in three replicates per treatment. The seeds of *Ricinus communis* were planted in each pot and analysed after 12 weeks of planting for heavy metals using AAS. Sequential extraction was carried out on the treated soil after the harvest with each extract further analysed for heavy metals using AAS.
Results: Application of cow manure significantly ($p < 0.05$) affected the redistribution and the

**Corresponding author: E-mail: ec.ezeudu@unizik.edu.ng;*

mobility of the heavy metals in the dump soil; as the concentration of the amendment increased, heavy metals in the mobile fractions reduced. 20% amendment had the best immobilization effect as the mobility factor decreased with increasing manure amendment. The mobility factors at 20% amendment were 18.34%, 15.82%, 5.23%, 15.86%, 25.56% and 12.81% for Cd, Cr, Cu, Mn, Pb and Zn respectively with the general trend of metal forms given as: residual > bound to organic > bound to Fe-Mn oxide > bound to carbonate > exchangeable.

Conclusion: Cow manure amendment of the dump soil decreased the availability of heavy metals for plant uptake; and the metal uptake generally decreased as percentage amendment increased. Cow manure is therefore a good immobilizing agent for remediation of Cd, Cr, Cu, Mn, Pb and Zn in polluted soils.

Keywords: Cow manure; soil amendment; metal immobilization; mobility factor.

1. INTRODUCTION

Contamination of the environment, and especially soils with heavy metals has been a century old problem, however there has been an alarming increase in the last five decades due to rapid urbanization, technological development and increased industrial use of many metal-containing materials [1]. Majid and Argue [2] and Zhou [3] have implicated heavy metals as major cause of human health problems in their reports, citing the increasing heavy metals in soils. Most metals in soil environment do not undergo microbial or chemical degradation like organic contaminants. So, they linger in large doses in the soils with a persistent ecotoxicity long after their introduction. Reports abound showing how heavy metals that remain in various ecosystems would seep into ground water or even channel into food chain by crops growing on such a soil [4].

The addition of organic matter for the remediation of contaminated soils has been used for many years to increase soil fertility, decrease soil heavy metal toxicity and generally enhance re-vegetation [5]. Walker et al. [6] observed that soil amendments through the addition of organic matter can reduce the bioavailability of heavy metals by changing their forms to fractions associated with organic matters or metal oxides or carbonates. Organic amendments can also improve soil aeration and enhance their water and nutrient holding capacities.

Several kinds of organic material have been used as amendments for the remediation of contaminated soils. Animal droppings, wood chips and saw dust, bio-solids, wood ash and compost derived from different sources are some of the favoured materials for soil amendment. The use of a range organic soil amendments including municipal solid waste, biosolids, cow manure, poultry manure, goat manure and pig manure for remediating heavy metals in contaminated soils have been investigated by various researchers [7-13]. A study by Zeng et al. [14] further used a combined amendment of bacteria and hydroxyapatite to immobilize cadmium in soils.

It however seems that animal droppings or manure has been the most utilized [15]. Davis and Wilson [15] further suggested that only aged manure be used for soil remediation purposes since fresh manure may harm plants due to elevated ammonia.

The in-situ immobilization of heavy metals using organic waste materials to remediate contaminated soil is a viable and cheap option; and so this study examines how amendment with cow manure can affect the heavy metal forms and distribution in the soil. Past studies have mostly looked at the wholesome use of manure from cows grown in a ranch setting with enhanced foods. This study examines the potential of cow manure from nomadic grazing.

2. MATERIALS AND METHODS

2.1 Sample Collection

Soil samples were collected from several dump sites at Nnewi, Anambra State at 15 cm depth using a spade into plastic bags and transported to the laboratory. The samples were air-dried, sieved with a 2mm sieve and then thoroughly homogenized before storing for further assessment. The cow manure used for the amendment was obtained from an open ranch in Awka, Anambra State, Nigeria. The fresh manure was dried, ground and stored for further use.

2.2 Pot Experiment

The experiment was conducted in a greenhouse. Pots of 14.0 cm diameter and a height of 12.0 cm were filled with 2.0kg of soil. Then, cow dung was added to the soil at 5%, 10% and 20% in three replicate treatments. The mixtures were then watered with deionized water and kept for 48 hrs in order to get equilibration of heavy metals between the amendments and the soils. The treatments were arranged in a completely randomized block design. Castor seeds (*Ricinus communis*) were sown in each of the amended soil and the seedlings later thinned down to one seedling per pot after germination. The plants were harvested after three months of germination by uprooting, then washed thoroughly with running water and deionized water respectively.

2.3 Plant Analysis

The harvested plants were dried for 72 hours at $60^{o}C$ and ground to powder. The plant samples were weighed (1g) into a digestion tube. 10mL of concentrated nitric acid was added and heated until black and brown fumes reduced. Concentrated sulfuric acid (10 mL) was added and heated until the solution turned colourless, 5mL of saturated solution of ammonium oxalate was also added to facilitate the removal of coloured nitro compounds. The mixture was heated till no brown fumes were observed [16,17]. They were later analyzed for heavy metals (Pb, Cd, Cr, Mn, Zn and Cu) using AAS (model: PG 990).

2.4 Soil Analysis

Standard methods were used to determine particle size while the pH value was then read on a pH meter. Organic carbon was determined using Walkley method [18].

2.5 Sequential Extraction

The sequential extraction procedure developed byTessier et al. [19] was used with the modification by Sebasthiar et al. [20], where residual metal content was determined in aqua regia digest in place of perchloric acid. The supernatants from each extraction stage was analysed for heavy metals using AAS (model: PG 990).

2.5.1 Exchangeable

1.0M $MgCl_2$ (8 mL) was added to 1g of the amended soil and pH adjusted to 7.0 with agitation for 1hr. The mixture was then centrifuged for 15 minutes. The supernatant was filtered into a polypropylene bottle for AAS analysis, while the residue was used for the next extraction.

2.5.2 Carbonate bound

1.0M NaOAc (8 mL) was added to the residue obtained from the exchangeable fraction above and then adjusted to pH 5.0 with concentrated acetic acid and agitated for 5 hours. The mixture was then centrifuged at 1500 rpm for 15 minutes. The supernatant was filtered into a polypropylene bottle for AAS analysis.

2.5.3 Fe-Mn oxides

0.04 M NH_2OH HCl (20 mL) in 25% HOAc was added to the residue obtained from the carbonate bound fraction and placed in water bath for 6 hours at $96\pm3^{o}C$. The mixture was brought out and centrifuged at 1500 rpm for 15 minutes. The supernatant was filtered into a polypropylene bottle for metal analysis.

2.5.4 Bound to organic

0.02 M HNO_3 (3 mL) and 5mL of 30% H_2O_2 adjusted to pH 2.0 was added to the residue obtained from the step above and mixture was heated to $85\pm2^{o}C$ for 2 hours. After cooling, 3 mL of 30% H_2O_2 was added and heated to $85\pm2^{o}C$ for 3 hours. The mixture was centrifuged at 1500 rpm for 15 minutes. The supernatant was filtered into a polypropylene bottle for metal analysis.

2.5.5 Residual fraction

Residue from the organic bound was digested with 8mL of aqua regia for 2 hours until the metals are totally dissolved.

2.6 Determination of Mobility Factor

Mobility factor is the percentage fraction of heavy metals that are mobile or available for plant absorption. It is calculated thus:

$$MF = (F1 + F2)/(F1+F2+F3+F4+F5) \times 100$$

F1 = exchangeable fraction, F2 = bound to carbonate, F3 = bound to Fe-Mn Oxide, F4 = bound to organic,

F5 = residual

2.7 Data Analysis

All data were analysed and presented using SPSS version 22. ANOVA was used to determine the variance between percentage manure amendments while Fischer's Least Significant Difference (LSD) was employed for multiple comparison at P<0.05.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties

Table 1 gives the physicochemical properties of the parent soil and amended soil. The parent soil was poorly sorted with a high sand fraction (93.8%) compared to the clay (2.8%) and silt fractions (3.4%). The pH of the parent soil sample in this study was 6.72±0.02 while for the amended soil with 5%, 10%, 20% of Cow manure gave a pH of 7.27 ±0.03, 7.35 ±0.03 and 7.49±0.01 respectively. They all fell within the range of 6.8 to 8.0 which has been recommended for optimum plant growth [21]. The total organic matter (%) values in the soil under investigation in this study was high 3.77±0.03. This significantly increased for the dump soil amended with 5%, 10%, and 20% of Cow manure to 4.64 ±0.01, 4.89 ±0.16 and 6.49 ±0.14 respectively. Some researchers argue that the high amount of organic matter in soils are responsible for increase in the soil pH [22]. The exchangeable cation Exchange capacity (ECEC cmol/kg) of the dump soil varied upon amendment with 5%, 10% and 20% of Cow manure having 14.81 ±0.07, 19.29 ±1.32 and 26.17±0.23 respectively.

The pH of the dump soil increased with increase in percentage amendment in the order, 20%>10%> 5%.This variation due to percentage amendment with Cow manure is statistically significant at p value < 0.05 and suggests that the increase in pH is as a result of amendment with cow manure as observed by other researcher [23]. Heavy metal ions in the solid phase may become available if there is change in soil cation, pH or oxidation-reduction potential. The organic matter content (%) of the dump soil increased with increase in percentage amendment with cow manures in the order; 20% > 10% > 5%. The variations in organic matter content (%) observed in this study due to percentage amendment with Cow manure is statistically significant at p < 0.05 suggesting that amendment of dump soil with manures at different percentages affected the organic matter content of the parent soil. This finding is in agreement with report that suggested that manure is an organic source of nutrients which increases the soil organic matter and enhances soil quality [24,25]. Soil organic matter is highly beneficial for the chemical, biological and physical properties of soils, thereby affecting the potential yield of soils. The poorly sorted nature of the various particle sizes indicated that these soils were not formed from the natural process of weathering of the underlying parent material but rather from deposited wastes. This finding is consistent with the report of Okoronkwo et al. [26] who noted the sand fraction in dump soils is usually higher than the clay and silt fractions.

3.2 Heavy Metals

Fig. 1 shows the heavy metal concentration of the cow manure used for the amendment. Tables 2-7 and Fig. 2 show the forms of the heavy metals in dump soil after amendment with 5%, 10% and 20% of cow manure. The distribution of concentrations in mg/kg of Cd, Cu, Zn, Cr, Mn and Pb in various soil fractions from exchangeable to residual fractions are presented in mean concentration ± standard deviation (% fraction).

3.2.1 Cadmium

The Cd distribution for 5% manure amendment gave a concentration (mg/kg), for the sequential fractions in the order of; residual > bound to organic > bound to Fe-Mn oxide > exchangeable > bound to carbonate. The mobile fractions of Cd available for plant absorption was 20. 26%. For 10% and 20% manure amendments, the order of sequential fraction observed was residual > bound to organic > bound to Fe-Mn oxide > bound to carbonate> Exchangeable in both cases, while the mobile fractions of Cd available for plant absorption were 23.42% and 18.35% respectively; the soil with 20% amendment showed the lowest mobile fractions of Cd available for plant absorption.

Table1. Physicochemical properties of parent's oil and amended soils

	Manure amendment			
Parameters	0%	5%	10%	20%
PH	6.72±0.02	7.27±0.03	7.35±0.03	7.49±0.01
% Organic matter	3.77±0.03	4.64±0.01	4.89±0.16	6.49±0.14
ECEC(cmol/kg)	14.58±0.07	14.81±0.07	19.29±1.32	26.17±0.23
%Sand	93.8±0.00	95.75±0.07	95.70±0.14	93.80±0.00
%Silt	2.8±0.00	3.35±0.07	3.30±0.00	3.40±0.00
%Clay	3.4±0.07	0.78±0.03	1.00±0.14	2.80±0.00

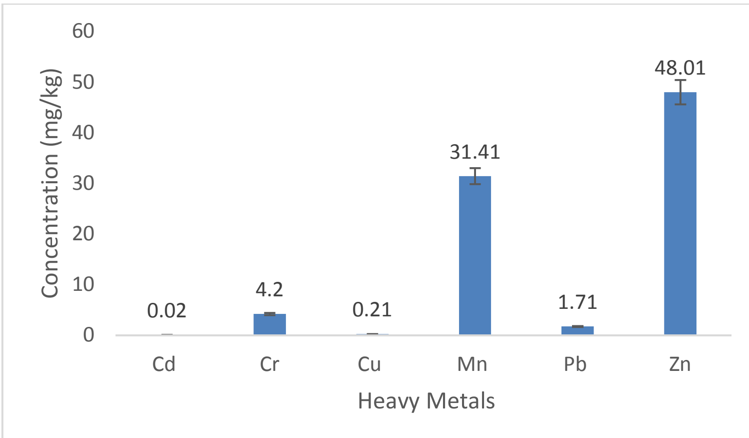

Fig. 1. Heavy metal concentration of cow manure

Table 2. Distribution of Cd in soil sample amended with 5%, 10% and 20% cow manure

Fraction	5%		10%		20%	
	Mean (mg/kg)	%Fraction	Mean(mg/kg)	% Fraction	Mean (mg/kg)	%Fraction
F1	5.70±1.30	11.68	5.22±1.76	10.17	3.33±0.99	5.89
F2	4.18±1.15	8.58	6.81±1.26	13.25	7.03±1.12	12.45
F3	8.61±2.0	17.65	9.52±2.81	18.54	11.35±2.53	20.11
F4	12.065±2.91	24.73	12.46±2.86	24.26	14.76±3.74	26.14
F5	18.23±3.49	37.37	17.36±3.54	33.79	19.99±6.81	35.4
Sum	48.79		51.38		56.47	
Mf%	20.26		23.42		18.34	

Key: F1=Exchangeable, F2= Bound to Carbonate, F3= Bound to Fe-Mn oxide, F4= Bound to Organic, F5= Residual, Mf= Mobility factor

Table3. Distribution of Cr in soil sample amended with 5%, 10% and 20% cow manure

Fraction	5%		10%		20%	
	Mean(mg/kg)	%Fraction	Mean(mg/kg)	%Fraction	Mean(mg/kg)	%Fraction
F1	3.45±0.48	13.47	3.18±0.71	16.15	3.60±0.44	9.49
F2	2.85±0.65	11.13	4.35±1.07	18.87	2.08±0.37	9.73
F3	6.62±1.91	25.83	5.27±1.26	9.74	4.90±1.58	16.12
F4	5.33±1.52	20.82	5.97±1.88	23.24	19.15±6.77	31.21
F5	7.37±2.03	28.76	6.55±1.86	32.01	6.18±1.13	33.45
Sum	25.62		25.32		35.92	
Mf%	24.59		29.76		15.82	

Key:F1=Exchangeable,F2=Bound to Carbonate,F3=Bound to Fe-Mnoxide,F4=Bound to Organic,F5=Residual, Mf=Mobility factor

3.2.2 Chromium

The highest fraction for Cr in dump soil amended with 5% of cow manure was obtained in the residual fraction (28.76%) while the lowest fraction was obtained bound to carbonate fraction (11.13%).The mobile fractions of Cr available for plant absorption in dump soil amended with 5%, 10% and 20% were 24.59%, 29.76% and 15.82% respectively. Sequential fraction for Cr concentration (mg/kg) followed the order; residual > bound to Fe-Mn oxide > bound to organic > exchangeable > bound to carbonate for 5% manure amendment; residual > bound to organic > bound to carbonate > exchangeable >bound to Fe-Mn oxide for 10% amendment and residual > bound to organic > bound to Fe-Mn oxide > bound to carbonate > exchangeable for 20% cow amendment.It was observed that the mobile fractions of Cr with respect to percentage amendment with cow manure followed the order; 10% > 5% > 20%.

3.2.3 Copper

The mobile fractions of Cu available for plant absorption decreased with increase in percentage amendment with cow manure in the order; 5% > 10% > 20%. The highest fraction obtained for Cu was in dump soil amended with 5% of cow manure (50.46%) while the lowest fraction was obtained in exchangeable fraction (2.28%) for 10% manure amendment. Based on the Cu concentration (mg/kg), the sequential fraction observed were in the order; residual > bound to organic > bound to Fe-Mn oxide > bound to carbonate > Exchangeable for 5% amendment and residual > bound to organic > bound to Fe-Mn oxide > bound to carbonate> exchangeable for 10% amendment.

3.2.4 Manganese

The highest fractions obtained for Mn were in dump soil amended with 5% and 20% of cow manure obtained in residual fractions; (42.71%) and 42.76% respectively. Based on the Mn concentration (mg/kg), the sequential fraction as observed followed the order; residual > bound to Fe-Mn oxide > bound to carbonate > bound to organic > exchangeable for 5% amendment; residual > bound to Fe-Mn oxide > bound to carbonate > bound to organic > exchangeable for 10% amendment and residual > bound to Fe-Mn oxide > bound to carbonate > bound to organic > exchangeable for 20% amendment. The mobile fractions of Mn available for plant absorption in dump soil amended with 5%, 10% and 20% of cow manure were 17.44%, 18.51% and 15.86% respectively.It was observed that the mobile fractions of Mn decreased significantly in soil amended with 10% followed by the soil amended with 5% of cow manure. The mobile fraction of Mn was lowest in the soil amended with 20% of cow manure.

3.2.5 Lead

The mobile fractions of Pb available for plant absorption in dump soil amended with 5%, 10% and 20% of cow manure were 27.86%, 27.33% and 25.56% respectively. It was observed that the mobile fractions of Pb decreased with increase in percentage amendment with cow manure in the order; 5% > 10% > 20%.The highest fraction obtained was in dump soil amended with 10% of cow manure bound to the residual fraction (33.03%). The Pb concentration (mg/kg) from the sequential fraction followed the order; bound to residual > Fe-Mn oxide > bound to organic > bound to carbonate > exchangeable for 5% amendment; residual > bound to Fe-Mn oxide > bound to organic > bound to carbonate > exchangeable for 10% amendment and residual > bound to Fe-Mn oxide > bound to organic > bound to carbonate > exchangeable for 20% amendment.

3.2.6 Zinc

The predominant form for Zn was in the residual fraction (62.84%) of the dump soil amended with 5% of cow manure. Amendment with 10% of cow manure showed similar trend with 5% amendment, while for the soil amended with 20% of cow manure, the order of sequential fraction observed was residual > bound to organic > bound to Fe-Mn oxide > bound to carbonate > Exchangeable. The mobile fractions of Zinc available for absorption decreased with increase in percentage manure amendment in the order; 5% > 10% > 20%.

Table 4. Distribution of Cu in soil sample amended with 5%, 10% and 20% cow manure

Fraction	5%		10%		20%	
	Mean(mg/kg)	%Fraction	Mean(mg/kg)	%Fraction	Mean(mg/kg)	%Fraction
F1	1.18±0.13	2.71	1.21±0.16	2.28	0.91±0.12	1.74
F2	1.61±0.17	3.7	1.88±0.85	3.55	1.82±0.29	3.49
F3	7.79±1.52	17.9	8.38±1.81	15.79	8.68±1.73	16.63
F4	10.99±1.92	25.24	16.18±3.99	30.5	17.94±3.12	34.39
F5	21.97±3.08	50.46	25.40±7.65	47.88	22.81±4.15	43.74
Sum	43.54		53.06		52.15	
Mf%	6.41		5.83		5.23	

Key: F1=Exchangeable, F2=Bound to Carbonate, F3=Bound to Fe-Mn oxide, F4=Bound to Organic, F5=Residual, Mf=Mobility factor.

Table 5. Distribution of Mn in soil sample amended with 5%, 10% and 20% cow manure

Fraction	5%		10%		20%	
	Mean(mg/kg)	%Fraction	Mean(mg/kg)	%Fraction	Mean(mg/kg)	%Fraction
F1	6.29±0.98	5.44	5.16±1.88	4.5	5.39±1.31	4.89
F2	13.87±2.95	12	16.06±4.18	14	12.09±4.75	10.97
F3	37.16±6.95	32.17	36.88±5.29	32.17	36.38±5.59	33
F4	8.87±1.55	7.68	8.03±2.22	7	9.24±2.33	8.36
F5	49.34±12.96	42.71	48.52±5.95	42.32	47.13±7.19	42.76
Sum	115.53		114.65		110.23	
Mf%	17.44		18.51		15.86	

Key: F1=Exchangeable, F2=Bound to Carbonate, F3=Bound to Fe Mn oxide, F4=Bound to Organic, F5=Residual, Mf=Mobility factor

Table 6. Distribution of Pb in soil sample amended with 5%,10% and 20% cow manure

Fraction	5%		10%		20%	
	Mean(mg/kg)	%Fraction	Mean(mg/kg)	%Fraction	Mean(mg/kg)	%Fraction
F1	18.53±5.53	11.83`	13.55±4.55	10.9	10.61±3.56	8.36
F2	25.1±5.48	16.03	23.84±5.18	17.42	21.83±5.57	17.2
F3	39.62±12.96	25.3	27.36±3.98	20	29.87±5.77	23.53
F4	28.09±2.08	17.94	26.89±7.55	19.65	25.63±6.63	20.19
F5	45.26±6.97	28.91	45.19±6.37	33.03	38.98±6.98	30.71
Sum	156.59		136.83		126.93	
Mf%	27.86		27.33		25.56	

Key: F1=Exchangeable, F2 = Bound to Carbonate, F3=Bound to Fe-Mn oxide, F4=Bound to Organic, F5=Residual, Mf=Mobility factor.

Table 7. Distribution of Zn in soil sample amended with 5%, 10% and 20% cow manure

Fraction	5%		10%		20%	
	Mean(mg/kg)	%Fraction	Mean(mg/kg)	%Fraction	Mean(mg/kg)	%Fraction
F1	4.19±1.19	3.91	3.65±0.70	3.26	3.13±0.99	2.26
F2	11.17±5.17	10.44	11.90±1.83	10.63	14.62±3.49	10.55
F3	7.33±1.33	6.85	10.21±3.01	9.12	14.82±4.13	10.7
F4	17.08±5.01	15.96	19.47±3.99	17.39	29.05±5.40	20.97
F5	67.25±6.25	62.84	66.73±14.33	59.6	76.92±12.55	55.52
Sum	107.02		111.95		138.56	
Mf%	14.35		13.88		12.81	

Key: 1=Exchangeable, F2=Bound to Carbonate, F3=Bound to Fe-Mn oxide,F4=Bound to Organic, F5=Residual, Mf=Mobility factor

3.3 Plant Metal Uptake (PU)

From Fig. 3, it was generally observed that as percentage manure amendment increased, mobility factor decreased as well as plant metal uptake. In most of the treatments, the amendment concentration with the lowest mobility factor recorded the lowest plant metal uptake similar to report by Alloway et al. [27]. They reported that the metal uptake from soil to plant was slow and explained that organic matter can introduce new binding sites to the soil and therefore fewer risk for plants, as compared to the soil without organic amendment. Uchimiya et al [28] and Wuana et al. [29] also discussed similar effects with soil amended with biochars and biosolids of poultry manure.

4. DISCUSSION

Fig. 1 shows that heavy metal concentrations in fractions of soil samples with cow manure amendment were lower when compared with un-amended soil and that the concentrations decreased with increase in percentage amendment. The amendment bound the metals and made them immobile. Addition of the amendment also brought about the increase in pH, ECEC and organic matter which also increased in values as amendment was added. The increase was highest in the amendment with 20% manure. This observation is similar to the report of Haroo et al. [30] that extraction of heavy metals reduced in contaminated soil upon addition of amendment. The reduction increased significantly as manure application rate increased It was also reported by Zobia et al. [7] that organic matter stabilizes heavy metals by forming stable complexes with them and that soil ability to reduce metal extractability increases with rising pH. The variations in properties of all the metals in each of the amended soil fractions was statistically significant ($p < 0.05$), implying that the amendment with cow manure affected the concentration of heavy metals in all the fractions. Similarly, it was observed that the percentage amendment with cow manure significantly affected the available forms of Cd, Cu, Mn, Pb and Zn ($P<0.05$). Multiple comparison between the three concentrations of cow manure revealed that 20% of Cow manure amendment has more effect on the forms of Cu and Zn, while 10% Cow manure has more effect on the forms of Cd.

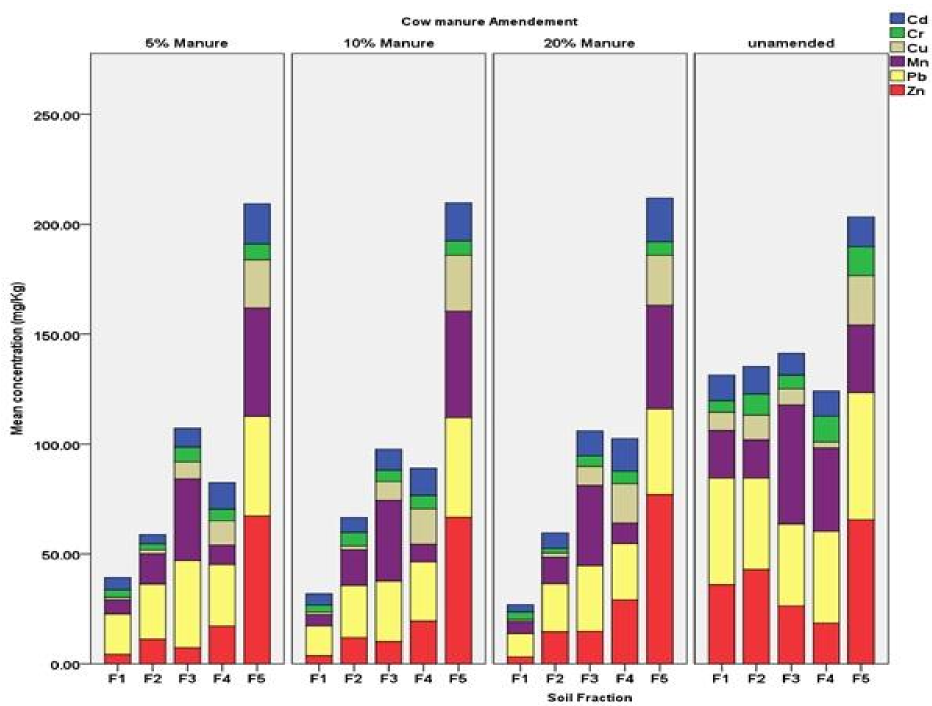

Fig. 2. Heavy metal concentrations in fractions of soil amended with cow manure

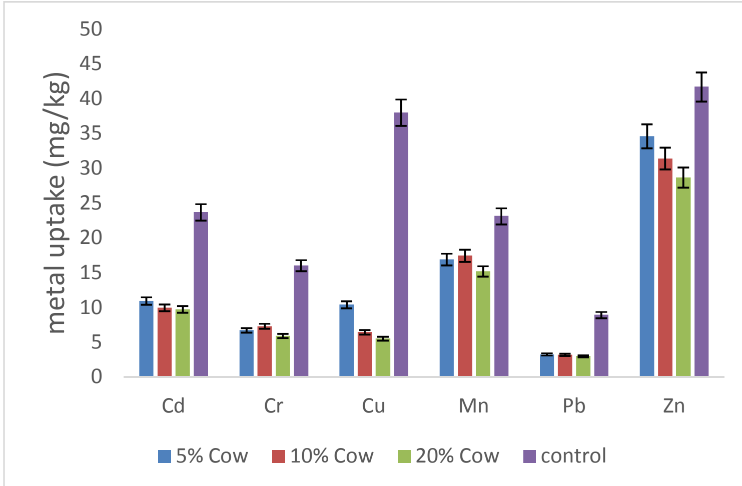

Fig. 3. Comparative effect of manure amendment on plant metal uptake (PU)

The speciation of heavy metals exerts strong influences on the mobility, bioavailability and toxicity of heavy metals in the contaminated soils [31,32]. It was also observed that there was reduction of the extractable fraction of all the metals after amendment with cow manure when compared with the extractable fraction of the un-amended soil. In this study, particularly on the effect of amendment with cow manure on the sequential fractions of heavy metal contaminated dump soils, it was observed that the concentrations of the heavy metals, followed the order; residual > bound to organic > bound to Fe-Mn oxide > bound to carbonate > exchangeable. This finding was corroborated by reports from Ghodsie and Ahmad [33] who stated that Fe-Mn oxide fraction exhibits the second most significant sink for Fe and Mn after residual fraction.

The residual fractions had the maximum amount of metal ions in them while the exchangeable fractions as well as those bound to carbonate have the minimum amount of metal ions in them. The mobile fraction: exchangeable and bound to carbonate, decreased in the amended soil as shown in Fig. 1. There is also a significant redistribution of heavy metals upon the addition of cow manure when compared with the un-amended soil. Mohammed et al. [34] reported similar trends for heavy metals in soils amended with nano- calcium silicate.

Generally, the mobile fractions of Cd, Cr, Cu, Mn, Pb, and Zn decreased upon amendment with cow manure when compared with the mobility factor of Cd, Cr, Cu, Mn, Pb, and Zn in parent soil. This study shows that in the amended soil, the metals were less mobile and therefore less available for plant absorption. The decrease in values for mobility factor of the amended soil maybe attributed to the high organic matter as well as the mildly alkaline conditions of the amended soil [35]. The immobilizing effect of cow manure (especially with 20% cow manure) on the dump soil in this study is consistent with the reports of various researchers [35,36,33] and [37]. Uwumarongie-Ilori et al. [38] also reported that Pb and Cr were bound mostly to the residual and organic fraction after amendment with different concentrations of cow manure. On the availability of Cd in soils, Khurana and Kansal [39] reported that addition of organic amendment decreases significantly the concentration of water soluble and exchangeable Cd but increases the amount of the metal into less mobile fractions (Fe-Mn oxide, organic and residual).

5. CONCLUSION

The study revealed that cow manure is a good immobilizing agent for remediation of heavy metal contaminated soils. The immobilization potential of the manure increased as their concentration in the soil was increased and the manure amendment significantly ($p < 0.05$) decreased the metal concentrations in the extractable fractions (exchangeable and bound to carbonate) when compared with un-amended soil leading to decreased plant metal uptake. A cow manure amendment of up to 20% is safe as it maintained the increasing immobilization effect. The concentrations of the heavy metals in different fraction followed the order: residual >

bound to organic > bound to Mn-Fe oxide > bound to carbonate > exchangeable.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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