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STABILIZATION OF HEAVY METALS IN CONTAMINATED SOIL USING A MIXTURE OF COW AND GOAT MANURE.

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ABSTRACT

The use of organic amendments, such as animal manure, has become a cost-effective alternative for decontaminating soil contaminated with heavy metals. In this study, a mixture of cow and goat manure was employed to determine its effectiveness. Physicochemical analysis of the parent soil revealed high concentrations of the targeted metals, including cadmium (61.62 mg/kg), lead (186.95 mg/kg), and zinc (226.85 mg/kg), among others. After amendment with 5%, 10%, and 20% (w/w) of a cow and goat manure mixture, Sequential extraction of the metals was performed to evaluate the redistribution of the metals in the soil. The results obtained showed that the concentrations of the metals were significantly reduced in the exchangeable and carbonate-bound fractions of all studied metals. In contrast, there is an increase in the organic-bound and residual fractions. For instance, a decrease in the mobility factor of cadmium from 40.84% in unamended soil to 19.86% in the soil amended with 20% manure was recorded. Similar reductions in the mobility's of chromium, copper, lead, manganese, and zinc were also observed. The redistribution of metals from mobile to immobile fractions indicates that the mixture of cow and goat manure is effective in stabilization of heavy metals in contaminated soils. This stabilization alters metal speciation, thereby decreasing their bioavailability. This study suggests that a cow and goat manure mixture offers a low-cost alternative in remediating these findings. Cow and goat manure mixtures can serve as a practical, low-cost alternative for in situ immobilization of metal-contaminated soils.

Keywords: Immobilization, speciation, mobility factor, heavy metal, sequential extraction.

1.0. INTRODUCTION

Unregulated disposal of heavy metals has led to the contamination of agricultural soils. This poses a significant risk to humans and animals living in the environment. It also affects farm productivity and food safety. Khan *et al*., (2020) reported that heavy metals such as cadmium, lead, etc., accumulate in soils as a result of anthropogenic activities. Such activities include: industrial discharge, mining, and indiscriminate dumping of refuse, among others. These metals do not biodegrade; instead, they persist in the environment and could become bioavailable for plant absorption.

The technology often used to remediate contaminated soils is very expensive. Alternatively, the use of in-situ stabilization using organic amendments presents a promising, cheaper and environmentally friendly alternative. Organic manures are not only readily available in rural communities but also capable of modifying soil properties and influencing the behaviour of heavy

metals through complexation, adsorption, and pH modification (Bolan *et al*., 2014).

Among organic amendments, cow and goat manure are abundant and rich in nutrients and organic matter. Their application can enhance cation exchange capacity (CEC), improve soil structure, and immobilize heavy metals by transforming them into less mobile or non-bioavailable forms (Wong *et al*., 2007). However, there is limited research on the combined use of different animal manures, such as cow and goat manure mixture and their synergistic effect on heavy metal stabilization in tropical soils.

This study evaluates the effects of a mixture of cow and goat manure on the stabilization and mobility of six heavy metals, Cd, Cr, Cu, Mn, Pb, and Zn, in dump soil. The objectives are to determine how amendment levels, 5%, 10%, and 20%, could influence the transformation of metal fractions and to assess their effectiveness in reducing metal mobility using the mobility factor (MF). The findings are expected to support the development of sustainable and low-cost soil remediation practices suitable for waste-impacted lands.

2.0. MATERIALS AND METHODS

Description of the Study Area

Soil samples for this study were collected at different refuse dump sites in Nnewi, figure 1. Nnewi is a significant town in Anambra State, Nigeria, renowned for its technological advancements. It lies between latitudes 5°05′N and 6°05′N, and longitudes 6°55′E and 7°00′E, covering an estimated land area of 72.52 km². Its boundary towns include Nnobi in the north, Utuh in the south, Amichi in the east and Ojoto in the west (Ezeomedo & Igbokwe, 2019).

There are four major villages in the town, namely; Otolo, Uruagu, Umudim, and Nnewichi. Kenechukwu *et al*., 2020 reported that the population of Nnewi is over 1,000,000 as at 2017. The town prides itself as one of the most industrialised cities in Nigeria. It is equally a commercial nerve centre in Anambra State, Nigeria. It is referred to as the "Japan of Africa" due to the establishment of numerous manufacturing industries, including car manufacturing plants, plastics, cosmetics, and metal fabrication (Onunkwo *et al*., 2014). These industries produce vehicles and parts, cables, batteries, paints, and household items, among others (Igalavithana *et al*., 2018).

Unregulated land use remains prevalent in the city, despite its economic viability. According to Okoronkwo *et al*., 2016, there is increased environmental stress as a result of industrial, commercial and agricultural activities. The concentrations of heavy metals in soils and water bodies within the area are high. This is due to the indiscriminate disposal wastes from industries, hospitals, schools and homes (Ogundiran & Osibanjo, 2009; Orisakwe *et al.,* 1999). Wang *et al*., (2019) and Le *et al*., 2018 reported that the lack of strategies in the management of wastes has become a serious concern to environmentalists. This is because negligence has facilitated the infiltration of toxic substances, such as heavy metals, into the soil and groundwater. This has raised a serious public health concern.

Environmental pollution in such commercial and Industrial areas is recognised as a global concern. Such concerns are more common where urbanization is prevalent. This is because urbanization usually outweighs infrastructural development and regulatory controls (Ramos *et a*l., 2020). The use of organic manure is effective and has therefore offered a better alternative in remediating heavy metals in contaminated soils, as it is cheap and readily available

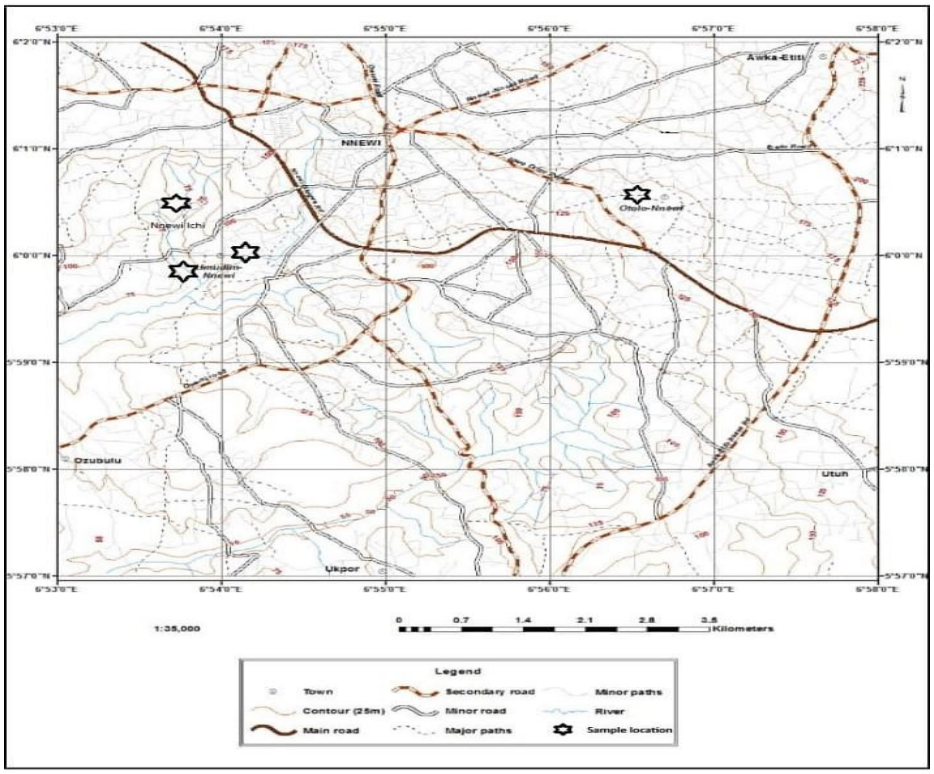

Figure 1: Map of Nnewi showing the locations of the refuse dump sites

Sample Collection

Manure from cows and goats was obtained from a livestock farm within the study area. They were air-dried and pulverized using a mortar and pestle to obtain a homogeneous fine powder. On the other hand, soil samples were collected from refuse dump sites across three major quarters of Nnewi: (Umudim, Otolo, and Nnewichi.

A clean stainless-steel spade was used to collect the soil samples at a depth of 0–15 cm. They were collected from each location into polyethylene bags and labelled. The samples were then transported to the laboratory, air-dried and sieved with a 2 mm sieve. The sieving process ensures that a uniform particle size is obtained. The processed soil samples were then thoroughly mixed and stored for physicochemical analysis and amendment.

2.2. Characterization of Samples

Physicochemical analysis was conducted on the parent soil to determine its physical and chemical properties. The pH of the soil was determined using a glass electrode pH meter in a 1:2.5 soil-to-water suspension ratio. Organic carbon content was determined using the Walkley–Black dichromate oxidation method. To obtain the value of organic matter, the value of organic carbon was multiplied by the factor 1.724. Adequate cation exchange capacity (ECEC) was determined by summing exchangeable bases and exchangeable acidity. Hydrometer method was used to determine the particle sizes. The total metals were determined using AAS. This was after the sample was first digested with a mixture of HNO_3 and $HClO_4$ in a 3:1 ratio.

2.4. Soil Amendment Procedure

The air-dried contaminated soil was amended with cow and goat manure in equal ratios (1:1 by weight) at application rates of 5%, 10%, and 20% (w/w). Each treatment was thoroughly mixed and incubated for 30 days under laboratory conditions at field-moisture capacity. Unamended soil served as the control. During incubation, the samples were periodically moistened to maintain consistent moisture levels.

2.5. Sequential Extraction of Heavy Metals

The sequential extraction of heavy metals in the amended and control soils was performed using a modified technique developed by Tessier *et al.,* (1979). This technique was used to determine the concentrations of metals in the exchangeable, carbonate-bound, Fe–Mn oxide-bound and organic-bound fractions of the metals. The residual fractions were determined using aqua regia digestion, following the method described by Sebasthiar (Sebasthiar *et al*., 2005).

Exchangeable Fraction: 8 mL of 1 M $MgCl_2$ was added to 1.00 g of air-dried soil. The pH was them adjusted to 7.0. The mixture was stirred for 1 hour at room temperature. The mixture was centrifuged at 3,000 rpm for 15 minutes. The supernatant was filtered through Whatman No. 42 filter paper into polypropylene tubes and stored at 4 °C. Heavy metal analysis using Atomic Absorption Spectroscopy. The residue was rinsed with deionized water and used for the next extraction step.

Carbonate-Bound: To the residue from the exchangeable fraction, 8 mL of 1 M sodium acetate was added. The pH was adjusted to 5.0 using glacial acetic acid. The solution was stirred for 5 hours and then centrifuged at 3,000 rpm for 15 minutes. The supernatant was filtered and stored for metal analysis.

Fe–Mn Oxide-Bound: The residue from the carbonate-bound was treated with 20 mL of 0.04 M hydroxylamine hydrochloride in 25% acetic acid. The mixture was heated for 6 hours in a water bath at 96 ± 3 °C with occasional shaking. On cooling, it was centrifuged at 3,000 rpm for 15 minutes, filtered, and stored.

Organic-Bound: 3 mL of 0.02 M nitric acid and 5 mL of 30% hydrogen peroxide were added to the residue. The pH was then adjusted to pH 2.0, and the mixture was heated to 85 ± 2°C for 2 hours. An additional 3 mL of 30% H_2O_2 was added. The heating was allowed to continue for the next 3. The sample was cooled, centrifuged at 3,000 rpm for 15 minutes, filtered and stored for metal analysis.

Residual Fraction: The residue obtained from the organic fraction was digested using 8 mL of aqua regia at 95 ± 5 °C for 2 hours to ensure complete dissolution of metals bound within the mineral matrix. The digest was filtered and stored for metal analysis.

2.6. Mobility Factor (MF)

Mobility factor (MF) was used to determine the relative mobility and bioavailability of each metal. It was calculated thus:

$$MF = \frac{F1+F2}{F1+F2+F3+F4+F5} \times 100$$

Where F1 and F2 are the exchangeable and carbonate-bound fractions, respectively. F3 is the Fe-Mn oxide bound fraction, F4 and F5 are bound to organic and residual fractions, respectively.

2.7. Statistical Analysis

All data were analysed and presented using SPSS version 22. ANOVA was used to determine the variance between percentage manure amendments. In contrast, multivariate analysis was used for the comparative immobilization effect of

different manure amendments and geochemical forms of heavy metals in the dump soil. Least Significant Difference (LSD) was employed for multiple comparison when the null hypothesis was rejected (if the P-value is less than 0.05).

3.0. RESULTS AND DISCUSSION

Physico-Chemical Properties of the Parent Soil:

The physico-chemical characteristics of the unamended soil sample are shown in Table 1.0. The table indicates that the soil sample has a sandy texture. It constitutes 93.8% sand, 3.4% silt and 2.8%. Sandy texture has low water and nutrient retention capacities. This is similar to the report of Li *et al*., (2021). Wang *et al*., (2020) reported that soils with a high percentage of sand fraction lead to high mobility of heavy metals as the binding sites of such soils are limited.

The pH of the soil is 6.72 ± 0.02. Sun *et al*., (2023) reported that this is within the range usually observed in anthropogenically influenced soils. This pH range agrees with the range reported by Ramos *et al*., (2020). This is significant for heavy metal behaviour because slightly acidic conditions enhance bioavailability of metals such as Cd^{2+}, Pb^{2+}, and Zn^{2}.

The Effective Cation Exchange Capacity (ECEC) of the unamended soil was 14.08 ± 0.07 cmol/kg. This indicates that the parent soil has a moderate capacity to retain and exchange metal cations. The value of 14.08 cmol/kg suggests that the soil requires amendment to improve its nutrient status. The low content of clay and organic matter results in the soil having a limited capacity to buffer against the leaching of metals. Li *et al*., (2019) reported that low organic carbon and high sand content corroborate the moderate ECEC level.

Zhang *et al*., (2023) also reported that soils with moderate ECEC have little ability to adsorb and retain metal ions. This usually results in higher metal mobility and bioavailability. This supports the finding of Ndung'u *et al*., (2021) that the use of organic amendments enhances both the organic matter content and cation exchange capacity of the soil. This improves its ability to immobilize heavy metals through adsorption, complexation and ion exchange mechanisms.

The values of organic carbon and organic matter contents were $2.19 \pm 0.02\%$ and $3.77 \pm 0.03\%$ respectively. These low contents are not sufficient to support effective metal immobilization. Organic matter is a complexing agent for heavy metals. Its low content may reduce the soil's buffering capacity against metal toxicity (Ndung'u *et al*., 2021).

The concentrations of heavy metals were high in the unamended soil: Zn (226.85 ± 1.63 mg/kg), Mn (217.75 ± 4.17 mg/kg), Pb (186.95 ± 3.46 mg/kg), Cd (61.62 ± 0.02 mg/kg) and Cu (61.90 ± 0.14 mg/kg). These values exceed permissible limits for agricultural soils (WHO & FAO, 2019). The high level of metals in the soil indicates a substantial degree of contamination. Igalavithana *et al*., (2018) attributed the high concentration of toxic metals in Nnewi soils to industrial effluents and indiscriminate dumping of waste materials. The concentration of Cr at 43.70 ± 1.84 mg/kg raises concern due to its toxicity and persistence in the environment. Okoronkwo *et al*., (2016) reported that Cr contamination in urban and industrial soils is linked to tanneries, metal plating and paint industries, which are commonly found in Nnewi.

Table 1.0: Physico-Chemical Properties of the unamended soil.

Physico-Chemical Properties	Parent Soil
pH	6.72±0.02
ECEC (cmol/kg)	14.08±0.07
Organic Carbon (%)	2.19±0.02
Organic Matter (%)	3.77±0.03
% Sand	93.8
% Clay	2.8
% Silt	3.4
Cd (mg/kg)	61.62±0.02
Cr (mg/kg)	43.70±1.84
Cu (mg/kg)	61.90±0.14
Mn (mg/kg)	217.75±4.17
Pb (mg/kg)	186.95±3.46
Zn (mg/kg)	226.85±1.63

Physico-Chemical Properties of Cow and Goat Manure:

Table 2.0 below shows the physico-chemical Properties of Cow and Goat Manure. From the result, it can be seen that the pH values of cow manure (9.21 ± 0.01) and goat manure (7.75 ± 0.01) were both alkaline. Cow manure was, however, more alkaline than goat manure. It has been reported by Sebasthiar *et al*., (2005) that when pH is alkaline, the immobilization of heavy metals will be enhanced. This is because alkaline pH causes metals to precipitate either as hydroxides or carbonates. The alkalinity of the manures suggests that both of them have the potential to increase the pH of acidic soils and, as a result, reduce the bioavailability of metals.

The organic matter content of cow manure ($29.35 \pm 0.01\%$) was slightly higher than that of goat manure ($24.38 \pm 0.01\%$). It interacts with soil to form stable organic metal

complexes (Ndung'u *et al*., 2021). The higher organic matter in cow manure suggests a more substantial potential for long-term stabilization; however, goat manure's slightly lower value is still significant enough to immobilize heavy metals.

It can also be seen that goat manure has higher ash content (3.37 ± 0.01%) than cow manure (2.80 ± 0.01%). Ramos *et al*., (2020) reported that mineral residue in ash can influence stabilization of heavy metals through mineralogical transformations.

Cow manure has a moisture content of 13.08 ± 0.01%. This was higher than that of goat manure, which was 3.87 ± 0.02%. The lower moisture content of goat manure is due to its drier nature as opposed to that of cow manure. The drier nature of goat manure makes it more convenient to handle, whereas the higher moisture content of cow manure ensures microbial activities are accelerated (Sun, 2023).

Heavy metal content was higher in goat manure when compared to cow manure. For instance, the concentration of cadmium was higher in goat manure (4.80 ± 0.01 mg/kg) than cow manure (0.02 ± 0.01 mg/kg). This finding agrees with the report of Hassan *et al.* (2020), indicating species and diet-related variability *in the* metal content of manure. The concentration of Pb (4.91 mg/kg vs. 1.71 mg/kg), Mn (72.33 mg/kg vs. 31.41 mg/kg), and Cu (1.02 mg/kg vs. 0.21 mg/kg) were also higher in goat manure. This elevated concentration of metals in goat manure suggests that it may increase metal loads in the soil when applied excessively.

Zn, on the other hand, was more concentrated in cow manure (48.01 ± 0.01 mg/kg) than in goat manure (39.92 ± 0.03 mg/kg). It is abundant in livestock feed and supplements. Its presence in manure is not uncommon. Even though zinc (Zn) is an essential micronutrient, its accumulation in soil can lead to phytotoxicity and microbial inhibition (Jiang *et al*., 2020).

The levels of Cr were similar in both manures (4.2 mg/kg). This concentration is within the permissible level for agricultural activities.

Table 2.0: Physico-Chemical Properties of Cow and Goat Manure.

Physico-Chemical Properties	Cow Manure	Goat Manure
pH	9.21±0.01	7.75±0.01
Organic matter (%)	29.35±0.01	24.38±0.01
Ash Content	2.80±0.01	3.37±0.01
Moisture Content	13.08±0.01	3.87±0.02
Cd (mg/kg)	0.02±0.01	4.8±0.01
Cr(mg/kg)	4.20±0.01	4.21±0.01
Cu (mg/kg)	0.21±0.01	1.02±0.03
Mn (mg/kg)	31.41±0.01	72.33±0.04
Pb (mg/kg)	1.71±0.01	4.91±0.01

Zn (mg/kg)	48.01±0.01	39.92±0.03

3.1. How Manure Mixture Influences Soil Physico-Chemical Properties

The influence of varying cow and goat manure mixture on soil physicochemical properties is shown in Table 3.0.

pH of the Soil

Upon the application of manure amendment, the soil pH increased. It was 6.72 ± 0.02 in the unamended soil, but after applying 5%, 10%, and 20% manure, it increased to 7.81, 7.49, and 7.33, respectively. This increase was as a result of the alkaline nature of the manure. According to the report by Hassan *et al*., (2020), animal manures introduce metal cations, which buffer soil acidity. Jiang *et al*., (2020) also reported that an increase in soil pH leads to a reduction in the mobility and bioavailability of most heavy metals.

Soil Organic Matter

It was observed that organic matter content increased with increasing manure amendment. It rose from 3.77% in the unamended soil to 5.04%, 7.95%, and 10.68% upon the addition of 5%, 10%, and 20% manure respectively. This trend shows that manure mixture is rich in organic matter, which usually improves soil structure and fertility. Li *et al*., 2029 reported that increase in soil organic matter improves microbial activity, formation of metal-organic complexes and water-holding capacity of soils.

Effective Cation Exchange Capacity

ECEC was improved after the manure mixture was applied. The improvement was significantly high at the 20% rate. It rose from 14.08 cmol/kg in the unamended to 23.77 cmol/kg. This increase is a result of the increased organic matter content and pH, which provide more active binding sites for nutrients and metal cations. Increased ECEC indicates an improved capacity of the soil to retain nutrients and immobilize heavy metals (Ndung'u *et al*., 2021).

Table 3.0: Effect of Cow and Goat Manure Mixture on the Soil Physico-Chemical Properties

	Manure Mixture Amendment			
	Control (0%)	5%	10%	20%
PH	6.72±0.02	7.81±0.03	7.49±0.01	7.33±0.17
%Organic matter	3.77±0.03	5.04±0.06	7.95±0.56	10.68±17
ECEC (cmol/kg)	14.08±0.07	13.46±0.65	14.81±0.75	23.77±0.29

Cadmium Fractionation and Mobility in Manure Mixture Amended Soil

Cadmium fractionation and mobility in the manure-amended soil are shown in Table 4.0. It highlights how cadmium was redistributed among geochemical fractions after amendment with different concentrations of the manure mixture. The sequential extraction provides an insight into the

mobility, bioavailability, and stabilization potential of Cd under organic amendment.

Exchangeable Fraction

This represents the most mobile fraction of metals. Metals in this fraction are readily available for plant absorption. In the unamended soil, the concentration of Cd in the exchangeable fraction was 11.70 mg/kg. This accounts for 19.74% of the total Cd in the unamended soil. This value decreased upon amendment with the manure mixture. It reduced to 7.13 mg/kg (16.49%), 6.12 mg/kg (12.03%) and 1.68 mg/kg (2.9%) at 5%, 10% and 20% manure application, respectively. This significant reduction, especially at 20% manure application, is an indication that the manure mixture has a strong immobilization ability. This observation supports the findings that organic amendments enhance adsorption and complexation of Cd, thereby reducing its bioavailability (Wang et al., 2019; Ndung'u *et al*., 2021; Jiang *et al*., 2020).

Carbonate-Bound Fraction

The concentration of Cd bound to carbonates also decreased across different levels of amendments. The highest reduction was recorded at 5% application. It reduced from 12.51 mg/kg, which represents 21% of the Cd in the unamended fraction, to 6.14 mg/kg. The reduction was less in 10% (17.18%) and 20% (16.96%) amendments. Wang *et al*., (2020) suggested that the redistribution is a result of the transformation of Cd into a more stable form due to the increased pH.

Fe-Mn Oxide Bound Fraction

It can also be seen from the table that the concentration of Cd bound to Fe-Mn oxide increased with amendments. It rose from 9.93mg/kg (16.75%) in the unamended soil to 7.83mg/kg (18.12%), 10.23mg/kg (20.12%) and 10.84mg/kg (18.76%) at 5%, 10% and 20% application, respectively. Lee *et al*., (2013) suggested that this observation may be due to increased redox buffering and precipitation of Cd-Fe/Mn complexes.

Organic-Bound Fraction

Upon amendment, the concentration of Cd bound to organic increased from 11.5mg/kg (19.4%) in unamended soil to 16.73mg/kg (28.95%) at 20% amendment. Animal manures contain high levels of organic matter, which promotes the formation of metal-humus complexes. This is a known mechanism for long-term immobilization of heavy metals (Sun *et al.*, 2016). Metals bound to the organic fraction are stable and not available for plant absorption.

Residual Fraction

In the residual fraction, metals are bound firmly in the mineral lattice. Such metals are stable and not bioavailable. The concentration of Cd in the residual fraction increased from 13.63 mg/kg (23%) in the unamended to 18.74 mg/kg (32.43%) at 20% amendment. The increase in residual fraction with amendment points to the fact that the manure mixture has the capacity to transform Cd from mobile form into immobile residual form (Wuana *et al*., 2012).

Mobility Factor

The mobility factor determines how stable a metal is in soils. Upon amendment, the mobility factor decreased significantly from 40.84% in the unamended to 19.86% at 20% amendment. This indicates that the manure mixture was effective in reducing the mobility of Cd. It should be noted that as the mobility of metals decreases, their bioavailability also decreases, making it difficult for plants to absorb them or for them to leach into groundwater. This is in agreement with the findings that the use of animal manures helps in heavy metal stabilization (Ndung'u *et al.,* 2021; Gupta *et al.,* 2013; Ramos *et al.,* 2020).

Table 4.0: Cadmium Fractionation and Mobility in Manure mixture amended Soil

Fraction	unamended (mg/kg)	%Fraction	5%(mg/kg)	%Fraction	10%(mg/kg)	%Fraction	20%(mg/kg)	%Fraction
F1	11.70±2.86	19.74	7.13±1.38	16.49	6.12±2.50	12.03	1.68±0.15	2.9
F2	12.51±1.78	21.11	6.14±2.38	14.21	8.74±1.99	17.18	9.80±1.58	16.96
F3	9.93±0.75	16.75	7.83±1.68	18.12	10.23±2.47	20.12	10.84±2.24	18.76
F4	11.50±2.01	19.4	9.43±1.56	21.82	11.94±1.39	23.47	16.73±2.68	28.95
F5	13.63±1.22	23	12.69±3.26	29.36	13.83±3.55	27.19	18.74±3.57	32.43
Mf%	40.84		30.7		29.21		19.86	

F1= exchangeable, F2= bound to carbonate, F3 = bound to Fe-Mn oxide, F4= bound to organic, F5= residua, MF= mobility factor

Chromium Fractionation and Mobility after Amendment.

Table 5 shows the sequential distribution of chromium in contaminated soil after amendment with different concentrations of cow and goat manure mixture. In the unamended soil, Cr was predominantly distributed in the residual (F5, 28.75%), organic-bound (F4, 25.35%), and carbonate-bound (F2, 20.93%) fractions. A substantial proportion remains in exchangeable and mobile forms (F1 + F2 = 32.34%). This observation indicates that the concentration of Cr in the mobile fraction is substantial and may pose environmental and health risks (Dai *et al*., 2022; Nurcholis *et al*., 2021).

After amendment with different concentration of manure mixture, it was observed that there was a redistribution of metals across different fractions. The concentration Cr in the residual fraction (F5) increased to 25.93 mg/kg (63.77%), 28.03 mg/kg (67.04%), and 29.27 mg/kg (70.9%) at 5%, 10% and 20% application, respectively. This indicates an increased stabilization of the metal. There was also a significant decline in bioavailable fractions, exchangeable and carbonate-bound forms. The decline was from 5.25 mg/kg (11.41%) and 9.63 mg/kg (20.93%) in the unamended soil to just 1.25 mg/kg (3.02%) and 1.00 mg/kg (2.42%) at 20% amendment, respectively.

This observation could be attributed to the combined effects of organic matter, increased pH and functional groups such as carboxyl and hydroxyl in the manure mixture. These properties promote the formation of Cr complexes, precipitation, or adsorption into stable forms (Kumpiene *et al*., 2008).

The mobility factor decreased significantly with increasing amendment levels from 32.34% in the unamended to 5.44% in the 20% amendment. This reduction highlights the efficiency of manure mixture in immobilizing Cr thereby limiting its ecological risk. Saha *et al*., (2020) reported a similar observation that organic amendments have the capacity to reduce the mobility of Cr in soils.

Table 5.0: Fractionation and Mobility of Chromium in Manure mixture amended Soil

Fraction	unamended (mg/kg)	%Fraction	5%(mg/kg)	%Fraction	10%(mg/kg)	%Fraction	20%(mg/kg)	%Fraction
F1	5.25±1.05	11.41	3.75±0.92	9.22	1.67±0.42	3.99	1.25±0.62	3.02
F2	9.63±1.29	20.93	1.95±0.54	4.8	1.12±0.93	2.67	1.00±0.83	2.42
F3	6.24±0.90	13.56	3.97±0.21	9.75	4.93±1.06	11.8	4.33±1.21	10.5
F4	11.67±2.07	25.35	5.07±0.98	12.46	6.07±1.06	14.51	5.43±1.25	13.16
F5	13.23±2.59	28.75	25.93±3.50	63.77	28.03±5.85	67.04	29.27±7.67	70.9
Mf%	32.34		14.02		6.66		5.44	

F1= exchangeable, F2= bound to carbonate, F3 = bound to Fe-Mn oxide, F4= bound to organic, F5= residua, MF= mobility factor

Chemical Fractionation and Mobility of Copper after Amendment.

The geochemical forms of copper among the various fractions in the unamended and amended soils are shown in Table 6. The exchangeable and carbonate-bound fractions of the unamended soil contributed 37.52% of total Cu. This, of course, makes the mobility of Cu high, posing an environmental risk. The remaining 62.48% of the total Cu was present in the stable fractions, with the residual fraction accounting for over 40%.

Manure amendments at increasing rates significantly altered the geochemical forms of Cu. For instance, the exchangeable fraction decreased from 15.88% in the unamended to 0.86% at 20% amendment. This shows that Cu was strongly stabilized. There was also a reduction in the concentration of carbonate-bound Cu from 21.64% to 11.07% after amendment, further indicating stabilization effects.

However, the percentage of Cu in Fe-Mn oxide and bound to organic fractions increased significantly with an increase in amendment levels. The organically bound Cu rose from 5.4% in the unamended to 31.58% at 5%, peaked at 30.52% at 10%. It then decreased to 27.97% at 20% amendment. Jiang *et al*., (2020) suggested that the increase was a result of the complexation of Cu with ligands present in the manure.

The concentration of Cu in the residual fraction remained high across all treatments. It increases with an increase in % amendment. The increase resulted in a significant reduction in the mobility factor, from 37.52% in the unamended to 9.69% at a

10% treatment. This shows that the mixture of cow and goat manure will be efficient in reducing the bioavailability of Cu.

Wang *et al*., (2019) and Ndung'u *et al*., (2021) reported similar trend. They highlighted that organic amendments are rich in humic substances and functional groups, which can immobilize Cu through many mechanisms. In the same light, Lee *et al.,* (2013) further suggested that the association of Cu with Fe-Mn oxides demonstrates redox-mediated adsorption or co-precipitation mechanisms.

Table 6.0: Copper Fractionation and Mobility in Manure mixture amended Soil

Fraction	unamended (mg/kg)	%Fraction	5%(mg/kg)	%Fraction	10%(mg/kg)	%Fraction	20%(mg/kg)	%Fraction
F1	8.28±1.07	15.88	0.92±0.12	2.59	0.60±0.09	1.6	0.40±0.09	0.86
F2	11.28±2.60	21.64	2.60±092	7.35	3.03±0.43	8.09	5.15±1.13	11.07
F3	7.30±0.34	13.99	4.91±1.63	13.85	4.90±0.99	13.09	9.81±1.60	21.1
F4	2.81±0.60	5.4	11.20±3.11	31.58	11.43±3.34	30.52	13.00±3.07	27.97
F5	22.47±3.41	43.1	15.83±1.03	44.63	17.50±4.12	46.71	18.13±4.13	39
Mf%	37.52		9.94		9.69		11.93	

F1= exchangeable, F2= bound to carbonate, F3 = bound to Fe-Mn oxide, F4= bound to organic, F5= residua, MF= mobility factor

Stability of Manganese in Amended Soil

The fractionation pattern of manganese in the studied soil indicates the effectiveness of manure mixture amendments in modifying Mn speciation and reducing its environmental mobility. In the unamended soil, a considerable proportion of Mn was found in the Fe-Mn oxide-bound and organic-bound fractions, with a smaller but still significant portion in the exchangeable and carbonate-bound forms. Onunkwo *et al*., (2014) reported that this fractionating pattern reflects the geochemical behaviour of Mn. The contamination of the soil by manganese (Mn) is likely due to industrial and waste disposal activities in the area.

The concentrations of Mn in mobile fractions decreased, while those in the immobile fraction increased, upon amendment. The presence of organic matter and mineral content of the manures was responsible for this reduction. It has been reported that organic matter improves soil structure and provides binding sites for metal

complexation (Wang *et al.,* 2019; Ndung'u*, et al.,* 2021). The residual fraction is considered to be the most stable and environmentally safe. The percentage amendments increased, whereas the mobility factor decreased.

These observations are in agreement with the report of Ramos *et al.,* (2020) that livestock manures can influence the redox conditions and organic matter composition of soil, thereby promoting the sequestration of Mn in less bioavailable forms. Jiao *et al., (2024)* further suggested that the observed reduction may be a result of complex interactions between microbial activity and humified materials, which form insoluble chelates with Mn.

Table 7.0: Fractionation and Mobility of Manganese in Manure mixture amended Soil

Fraction	unamended (mg/kg)	%Fraction	5%(mg/kg)	%Fraction	10%(mg/kg)	%Fraction	20%(mg/kg)	%Fraction
F1	21.64±3.54	13.37	20.57±2.95	14.06	24.13±5.81	12.95	19.67±2.12	10.42
F2	17.38±1.73	10.74	4.47±0.95	3.05	5.90±1.56	3.17	8.00±1.20	4.24
F3	54.27±6.31	33.52	22.30±4.07	15.25	44.37±4.20	23.81	41.63±6.31	22.06
F4	37.90±4.41	23.41	44.47±6.23	30.4	48.43±5.89	26	53.47±9.23	28.33
F5	30.70±4.19	18.96	54.47±7.53	37.24	63.47±10.62	34.07	65.97±13.85	34.95
Mf%	24.1		17.11		16.12		14.66	

F1= exchangeable, F2= bound to carbonate, F3 = bound to Fe-Mn oxide, F4= bound to organic, F5= residua, MF= mobility factor.

Immobilization Effect of Manure Mixture Amended Soil on Lead

The immobilization effect of a mixture of cow and goat manure is presented in Table 8. The concentration of Pb was redistributed as a result of manure amendments. In the unamended soil, the concentration of Pb was majorly in the exchangeable and residual fractions, contributing more than 40% of the total Pb content. The implication of the exchangeable fraction amounting to 21.37% is that there will be a high mobility of Pb, which will lead to a risk associated with Pb in its unamended state (Okere *et al.,* 2020).

Upon amendments with manure mixture, the concentration of extractable Pb reduced. The reduction followed the increase in the amendment. The exchangeable fraction decreased from 21.37% in the unamended soil to 8% at 20% amendment. The bound carbonate fraction was also reduced from 18.38% to 12.79%. This reduction is a result of improved Pb stabilization through

complexation and co-precipitation (Jiao *et al.,* 2024).

The residual fraction of the metal increased from 25.47% in the unamended soil to 44.84% at 20% amendment. This increase indicates that Pb was strongly stabilized, making it challenging to get into the food chain. Jiang *et al.,* (2020) attributed the strong stabilization to Pb adsorption to stable mineral surfaces and the formation of strong organic-Pb complexes.

Fe-Mn oxide-bound and organic-bound also experienced increases in Pb concentration. This is further proof that animal manures have the capacity to introduce certain functional groups, such as COOH, –OH and $–NH_2$, which enhance sorption processes (Wang *et al.,* 2019). These geochemical fractions typically act as sinks, mitigating Pb stability and bioavailability.

The mobility factor of Pb, on the other hand, decreased from 39.75% in the unamended soil to 20.79% at 20% amendment. This is an indication that organic amendments through stabilization reduce the risks posed by Pb in the environment. The report of Yuan *et al.,* (2023) that organic amendments reduce Pb mobility by enhancing its retention in stable soil pools confirms these findings.

Table 8.0: Lead Fractionation and Mobility in Manure mixture amended Soil

Fraction	unamended (mg/kg)	%Fraction	5%(mg/kg)	%Fraction	10%(mg/kg)	%Fraction	20%(mg/kg)	%Fraction
F1	48.49±3.15	21.37	23.90±2.99	14.11	14.30±1.30	8.26	13.77±2.25	8
F2	41.70±4.44	18.38	22.47±3.36	13.26	24.00±3.20	13.86	22.00±4.40	12.79
F3	37.17±3.98	16.38	24.60±3.31	14.52	25.17±9.66	14.54	26.36±5.36	15.32
F4	41.77±5.02	18.41	25.00±4.00	14.76	29.07±11.65	16.79	32.77±6.06	19.05
F5	57.79±7.43	25.47	73.47±12.94	43.36	80.60±15.25	46.55	77.13±11.22	44.84
Mf%	39.75		27.37		22.12		20.79	

F1= exchangeable, F2= bound to carbonate, F3 = bound to Fe-Mn oxide, F4= bound to organic, F5= residua, MF= mobility factor.

Zinc Stabilization Trends

The effect of cow and goat manure mixture on the geochemical forms of zinc in contaminated soil is presented in Table 9 below. The table clearly shows how Zn transforms from mobile to a more stable form upon the addition of different levels of amendments. In the unamended soil, Zn was highly mobile with over 41% of the total

metal present in the mobile fraction. This indicates that the metal is highly mobile in the unamended soil and as a result will pose a significant ecological risk. (Zhang, 2021).

On application of varying levels of manure mixtures, the exchangeable Zn decreased from 19.04% to 1.05% at 20% amendment. A similar observation was also recorded in the carbonate-bound fraction. These observations corroborate the findings of Rehman (2022) and Huang (2019), which reported that there were significant reductions in mobile fractions of Zn upon amendment with organic manure.

Zn present in the Fe-Mn oxide and organic fractions increased across all amendment levels. This suggests that there was enhanced stabilization, which may be through adsorption and complexation. At 20% amendment, Zn bound to organic matter increased to 22.4%, while Fe-Mn oxide-bound Zn reached 16.31%. These are pointer to the fact that humic substances and redox oxides provided effective sorption sites for Zn (Chen, 2021).

Metals in the residual fraction are often considered the most stable form. The concentration of Zn in this fraction increased from 34.64% in the unamended to 53.86% at 20% amendment. This transformation into stable form reflects long term immobilization potential of the amendment strategy. This aligns with the findings earlier reported by Ezeudu *et al.,* (2021) that Zn strongly associates with residual fractions after organic manure treatment.

Across treatments, there was steady reduction in mobility factor from 41.66% to 9.62%. This indicates that the mixture of cow and goat manure is very efficient in reducing the environmental risk posed by Zn in contaminated soils. Manure mixture amendment not only enhances Zn stabilization, it also also minimizes its leaching and uptake potential by plants, a key goal in the remediation of metal polluted soils.

Table 9.0: Fractionation and Mobility of Zn in Soil Amended with a mixture of Cow and Goat Manure.

Fraction	unamended (mg/kg)	%Fraction	5%(mg/kg)	%Fraction	10%(mg/kg)	%Fraction	20%(mg/kg)	%Fraction
F1	36.03±4.13	19.04	4.30±0.94	4.39	4.02±0.92	3.26	1.50±0.26	1.05
F2	42.81±5.19	22.62	5.93±1.02	6.06	9.13±1.41	7.4	12.30±3.32	8.57
F3	26.36±4.47	13.93	15.54±5.66	15.88	19.92±3.92	16.14	23.39±4.98	16.31
F4	18.48±3.46	9.77	20.28±7.85	20.72	23.87±4.52	19.35	32.12±4.00	22.4

F5	65.56±7.56	34.64	51.82±11.63	52.95	66.46±17.24	53.86	74.10±10.46	51.67
Mf%	41.66		10.45		10.65		9.62	

F1= exchangeable, F2= bound to carbonate, F3 = bound to Fe-Mn oxide, F4= bound to organic, F5= residua, MF= mobility factor.

Comparative Effectiveness of Amendment Levels

An increase in the levels of amendment consistently increased the stabilization across all metals. The 20% amendment reduced the mobility factor more effectively. It also significantly increased the residual fractions. The mobility factor of the heavy metals under different amendment levels is shown in Figure 2 below.

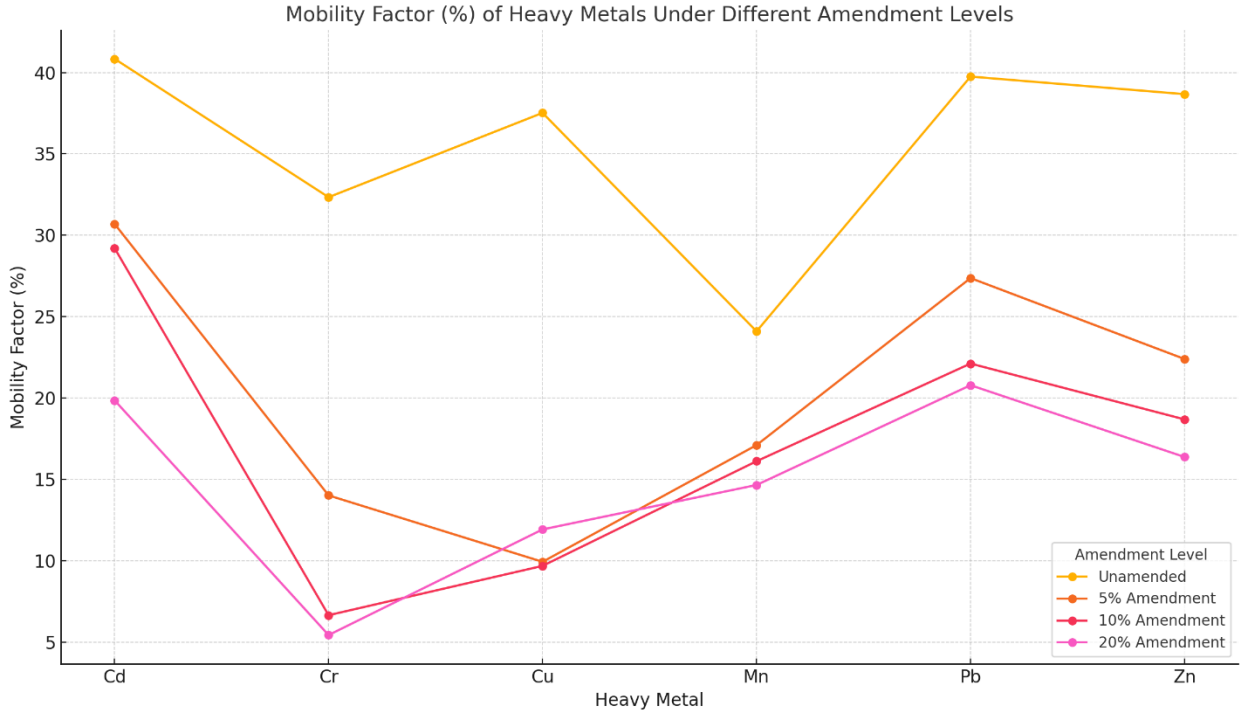

Figure 2: Mobility Factor of Heavy Metals Across Different Amendment Levels.

As shown in Figure 2, the chart above, the mobility of all metals decreased with increasing amendment level. The 20% amendment has the highest immobilizing effect on Chromium and Copper, as they have the lowest mobility factor. The graph generally shows that the application of cow and goat manure mixture reduces the mobility of all the studied metals. The manure mixture could therefore be used as a sustainable amendment to immobilize toxic metals in contaminated soils.

5.0. CONCLUSION

This study demonstrated that the mixture of cow and goat manure in the ratio of 1:1 is effective in stabilization of heavy metals. The manure mixture enhanced the physico-chemical properties of the soil such as pH, organic matter content, ECEC, ash content

etc. These improved properties contributed immensely to the reduction of metal mobility.

Sequential extraction of the metals showed that the mobile fractions of the metals were reduced upon amendments. These mobile fractions were converted to more stable fractions through complex interactions between the metals and organic matter. This conversion to a more stable form further increases when the level of the amendments is increased. The mobility factor of all the metals decreased significantly, with chromium having the most pronounced stabilization.

Application of cow and goat manure mixture provided synergistic stabilization effects likely due to their complementary chemical compositions. Cow manure provided high pH buffering and organic matter, while goat manure contributed greater mineral content and binding sites. These results confirm that organic manures are highly effective in mitigating the environmental risks associated with soils contaminated by heavy metals.

Recommendations

Although the results obtained from this study are promising, it is only a laboratory study. Field scale study should be conducted so as to determine the long-term effect of the manure mixture amendments on heavy metal contaminated soils under field conditions. There is also the need to do a phytoremediation study in a contaminated soils amended with the manure mixture in order to confirm the reduction in bioavailability of the metals. Furthermore, advanced spectroscopic techniques should be employed to elucidate the molecular-level interaction between manure constituents and metals.

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