

Sequential Fractionation of Heavy Metals from Flooded and non-flooded Soils in Obunagha Community, Bayelsa State, Nigeria

Original Research Article

ABSTRACT

Soil samples from flooded and non-flooded areas of different farmlands in Obunagha community, Bayelsa State were collected for this study. The aim of the study was to investigate the chemical fractionation and bioavailability of Cr, Cd, Zn, Ni, & Fe in flooded and non-flooded farmlands. The soil samples were fractionated into six chemical fractions, each containing different heavy metal concentrations and analyzed using flame atomic absorption spectrophotometer. The highest average concentration for Cadmium (Cd) is 1.50g/kg, Zinc (Zn) is 7.53g/kg, Nickel (Ni) is 10.54g/kg, Iron (Fe) is 9.52g/kg, and Chromium (Cr) is 12.62g/kg all from the flooded areas of the farmlands. Sequential extraction showed heavy metals distributed throughout all extraction steps, with the water-soluble fraction prevailing, potentially increasing the mobility and bioavailability of these metals. The % bioavailability ranged from 37.98% – 90.00%. The results indicated also that the average concentration of the metals in flood affected farmland were more than the non-flooded areas. The results indicated that floods affect farmland metal content by altering contaminant bioavailability, causing adverse environmental effects. Also, the results of the heavy metals analyses revealed that the levels of nickel, zinc, chromium, cadmium and iron in all the farmland soil samples are above the maximum allowable concentration for heavy metals in soil set by WHO Guidelines provided. Hence, the farmland soils are not safe for agricultural activities. We therefore, recommend regular monitoring of the soils to prevent excessive build-up of these toxic heavy metals.

Keywords: Heavy metals, sequential extraction, flooding, farmlands, bioavailability, Obunagha

1.0 INTRODUCTION

Human activities interacting with severe climatic factors have led to land degradation, including soil erosion [1]. Flood-induced soil erosion poses a significant threat to the social and economic well-being of Bayelsa State residents in Nigeria. Flood refers to an extensive overflow of water from sources like rivers, ponds, or ruptured pipes, submerging formerly dry regions [2,16,17]. This happens when soil and vegetation can't absorb all the water; excess water then runs off the land in amounts too large for stream channels or natural ponds and constructed reservoirs like dams to handle [2]. In addition, flooding significantly contributes to the transportation of trace elements linked with particulate matter.

Soils serve as the primary storage for various harmful components, encompassing both chemical and biological substances, such as heavy metals. Heavy metal pollution in the natural environment is a global issue due to the indestructible nature of these metals and their toxic effects on living organisms when concentration levels surpass permissible limits [3]. Heavy metals form diverse associations with soil components, influencing their mobility and availability [4]. The sequential extraction method is commonly employed to determine trace element fractionation in soils and sediments. Considerable attention has been directed towards examining the overall metal content of soil, with the analysis of speciation

(bioavailability) of these metals being a valuable analytical tool [5]. Consequently, there has been a rise in studies utilizing sequential extraction techniques to investigate the speciation or chemical forms of heavy metals in polluted soils. This is attributed to their ability to provide insights into metal affinity to soil components and the strength of their binding to the soil matrix [4]. Sequential extractions offer insights into the dynamic and inert portions of heavy metals in soils, facilitating assessment of both the present and potential mobility of the elements under investigation. Understanding the phases containing heavy metals and their solubility in water-based fluids allows for inference regarding the potential mobility and bioavailability (lability) of harmful metals[6].

The aim of this study was to determine the level of Cr, Cd, Zn, Ni & Fe contamination and mobility in selected flooded and non-flooded soils in Obunagha Community, Bayelsa State using the sequential extraction method. This study will elucidate the chemical behavior of heavy metals in soil environments, serving as the cornerstone for assessing the risk posed by soil contamination due to heavy metals following flooding incidents.

2.0 Method

2.1. Description of Study Area

Obunagha community in GbarainClan, is located in Yenagoa LGA, Bayelsa State, Nigeria (Fig 1), that lies latitudes 4°59'N - 5°28'N and longitudes 6°15'E - 6°21'E. The community lies to the north of Okolobiri, to the south of Tunuama, to the east of the Opokuma clan, and to the west of the Onopa village in Atisa Kingdom. The area experiences average farming and commercial activities. The community also experiences adverse flooding during raining seasons. ObunaghaCommunity experience flooding due to the overflow of river Nun and adjoining Taylor's creek. Figure 1 is a map showing the Obunagha creek, LNG road, host community. Figure 2 shows the GPS maps of the sampling sites.

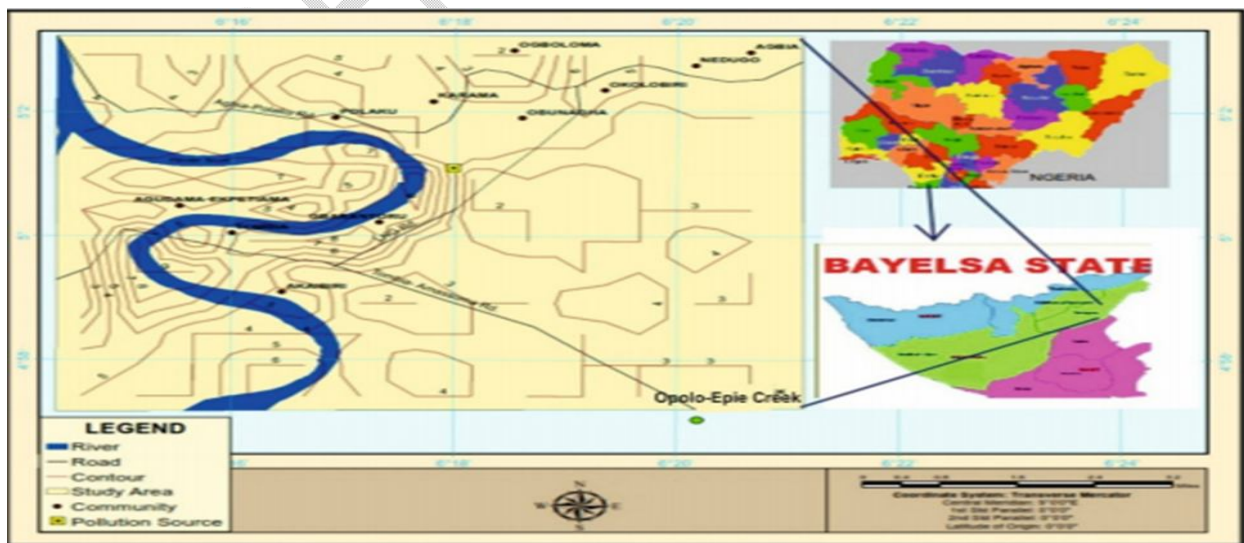


Fig 1: Location Map of the Study Area.

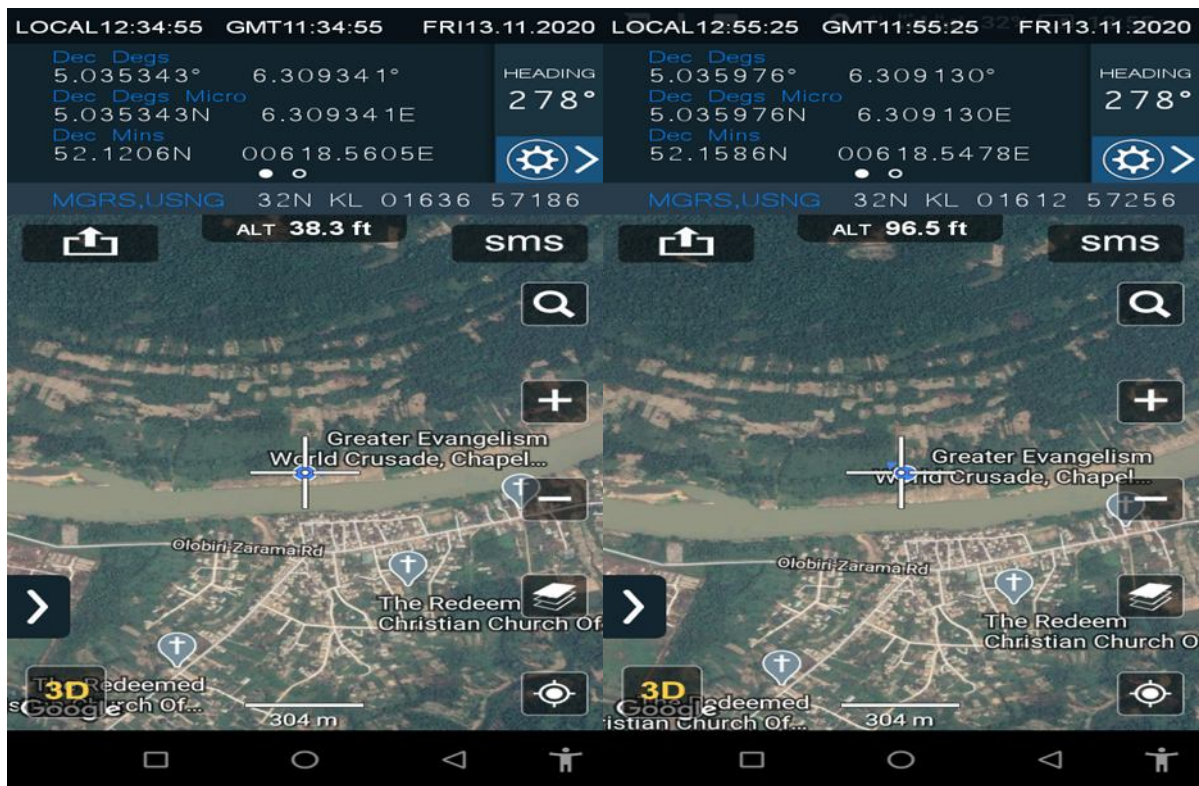


Fig 2: Showing the GPS positions of the sampling sites.

2.2. Chemicals, reagents and instruments

Equipment/instruments employed in this study included: Atomic Absorption Spectrometer (AAS model: S4 = 71096; for toxic heavy metal determination of soil samples), pH meter (for pH determination), Conductivity meter (for determination of conductivity of the soil). The common laboratory apparatus which was used during the study include; different sized beakers, funnels, Filter paper- Whatman, masking tape, centrifuge, shaker, droppers, glass pipettes, spatula, pestle and mortar, measuring cylinders, reagent bottles, volumetric flasks, soil auger, stirrer, Water bath, Centrifuge, polyethylene bags, plastic sieve, analytical balance, and conical flasks.

All chemicals utilized were of analytical reagent grade. Deionized water and distilled water were exclusively employed for all preparation and dilution procedures throughout the study. Magnesium chloride ($MgCl_2$), Acetic acid (CH_3COOH), Hydroxylamine hydrochloride ($NH_2OH.HCl$), Sulphuric acid (H_2SO_4), Nitric acid (HNO_3), Sodium ethanoate (CH_3COONa), Ammonium acetate (CH_3COONH_4), Barium chloride dihydrate ($BaCl_2.2H_2O$), Magnesium sulphate ($MgSO_4$), and Potassium chloride (KCl) were used for the study.

2.3 Sample Collection

Samples were collected using soil auger from different farm lands in Obunagha, Yenagoa Local Government Area of Bayelsa State, Nigeria from two different farms at different depths labeled.

Farm 1

- FMIA - 2mm deep (flooded Area)
- FMIB - 150mm deep (Flooded Area)
- FMIC - 2mm deep (Non-flooded Area)
- FMID - 150mm deep (Non-Flooded Area)

Another farmland labeled Farm 2

- FM2A - 2mm deep (Flooded Area)
- FM2B - 150mm deep (Flooded Area)
- FM2C - 2mm deep (Non-Flooded Area)
- FM2D - 150mm deep (Non-Flooded Area)

2.4 Preparation of Sample

The samples were air dried about seven (7) days in plastic containers, crushed using a ceramic mortar and pestle, and sieved using a 2mm plastic sieve. The finely sieved samples were stored and well labeled in plastic containers for laboratory use.

2.5 Sequential Extraction

Trace metals found in the soil from different soil samples were sequentially extracted into specific chemical forms (fractions). Each sample was treated in triplicate. The method of Horowitz [7] which is a

modified version of Tessier *et al.*, [8] was used for the chemical fractionation of metals (Cr, Cd, Ni, Zn, Fe) in the soil. The procedures were carried out in six fractions as follows:

- Fraction 1 (F1) = Water Soluble Metals
- Fraction 2 (F2) = Exchangeable Metals
- Fraction 3 (F3) = Bound to Carbonate metals
- Fraction 4 (F4) = Bound to Fe-Mn oxides
- Fraction 5 (F5) = Bound to Organic carbon metals
- Fraction 6 (F6) = Residual Metals

2.5.1 Determination of Water-Soluble Metals (F1)

1.0g of air-dried soil samples (from FM1A, FM1B, FM1C, FM1D, FM2A, FM2B, FM2C, FM2D) were placed in a prewashed 50mL poly carbonate centrifuge tube. The soil samples were extracted with 20mL de-ionized water added into the centrifuge 2000 rpm for 2hours.

The supernatants from each tube were gradually decanted in a prewashed and well labeled plastic container with addition of 0.5mL of concentrated HNO₃ and set aside for AAS determination. Then the residues were kept for the next procedure (Fractions 2).

2.5.2 Determination of Exchangeable Metals (F2)

8.0mL of 1.0M MgCl₂ were added to the residues from Fraction 1 (F1) at room temperature at pH7. The mixtures were continuously agitated for 1 hour. The separation of the extracts from the residue was achieved through centrifugation at 2000 rpm for 1 hour. The supernatants liquid was decanted into a pre-washed and well labeled plastic container, with addition of 0.5mL of concentrated HNO₃ and set aside for AAS analysis. The residues were meticulously rinsed by adding 20 mL of deionized water, shaking for 20 minutes, followed by centrifugation, and then discarding the supernatant. This fraction demonstrates changes in water ionic compositions and sorption processes.

2.5.3 Determination of Bound to Carbonate Metals (F3)

The metals attached to carbonates were extracted by mixing 8.0 mL of 1 M CH₃COONa with the (F2) residue in a tube. The pH was regulated to 5 with acetic acid at room temperature and kept under continuous agitation for 5 hours. Subsequently, the extracts were separated from the residue through centrifugation at 2000 rpm for 1 hour. The supernatant liquid was decanted into a pre-washed plastic container well labeled with addition of 0.5mL of Concentrated HNO₃ into the liquid and set aside for AAS determination.

The residues underwent a thorough cleansing process, with the addition of 20mL of distilled water, agitation for 20 minutes, followed by centrifugation, decantation, and subsequent disposal. This fraction concerns the concentration of the sediments which varies with pH.

2.5.4 Determination of Metals Bound to Iron and Manganese Oxides (F4)

These were extracted by adding 20ml of 0.04M Hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in 25% (v/v) acetic acid into the residues from (F3) adjusted to 96°C using water bath. The mixtures were continuously agitated for 6 hours and separated by centrifugation at 2000rpm for 1 hour.

The supernatant liquid was decanted into the washed plastic containers and 0.5mL concentrated HNO_3 were added into the supernatant liquids and set aside for AAS Analysis. The residues were thoroughly washed using 20mL distilled water and agitated for 20 minutes centrifuged decanted and discarded.

2.5.5 Determination of Metals Bound to Organic Carbon (F5)

Metals bound to organic carbon was extracted with 3.0mL of 0.21M HNO_3 and 5.0ml of 30% H_2O_2 into the residues from fraction 4 (F4). The pH was adjusted to 2 using 2mL of concentrated HNO_3 . The mixtures were continuously agitated for 2 hours while being heated in a water bath to 85°C . The mixtures were digested the second time with 3.0mL aliquots of 30% H_2O_2 (Hydrogen peroxide) added to the residue (adjusted to pH2 with addition of HNO_3) and the mixtures were heated again using water bath to the temperature of 85°C with continuous agitation for 3 hours. The mixtures were cooled and 5.0mL of 3.2M ammonium acetate (CH_3COONa) in 20% (v/v) the sample solutions were rigorously shaken for 30minutes after the sample solutions were diluted with 20.0mL of distilled water. The solution was centrifuged in 2000rpm for 1 hour and decanted and 0.5mL HNO_3 added to the supernatant liquid and set aside for AAS analysis in a prewashed contained well labeled. The added CH_3COONa were used to avoid adsorption of extracted metals on the oxidized soil sample.

2.5.6 Determination of Residual Metals (F6)

This fraction describes the residues after the first five fractions which contain mainly primary and secondary minerals: probably holding trace metals within their crystal structures. Residual metals were extracted by pouring 20 mL of 4 mol/dm³ HNO_3 into the residue from fraction five (F5), previously rinsed with distilled water. The solutions were preheated to 80°C using water bath and agitated for 16 hours. The supernatant liquids were extracted using centrifugation procedures at 2000rpm for 30mins. The supernatant liquid was decanted and added 0.5mL of concentrated HNO_3 and set aside for AAS Analysis.

2.6 Chemical Analysis

The supernatant solutions from stages (F1) to (F5) along with the residual digest (F6) underwent analysis for trace elements including chromium, cadmium, nickel, zinc, and iron. This analysis was carried out using the Perkin Elmer Atomic Absorption Spectrophotometer (model 403). Each extraction process was replicated three times.

%Bioavailability

The %Bioavailability gives the amount of metal that is available for plants; it is given in equation1.

$$\%Bioavailability = \frac{\sum \text{concentration of metal n in fractions 1 and 2}}{\sum \text{concentration of metal n in fractions 1 - 6}}$$

2.7 Data Analysis

Three sets of samples were prepared to ensure robust data for statistical analysis. The statistical analysis encompassed calculations for mean, standard deviation, and analysis of variance (ANOVA). Specifically, the data on heavy metal concentrations for each metal underwent spatial variation analysis employing one-way ANOVA within the SSPS version 20 package. Results interpretation adhered to a single level of significance. Additionally, bar charts were employed to facilitate comparison of the data.

3.0 RESULTS AND DISCUSSIONS

3.1 Sequential extraction

The sequential extraction scheme proves valuable for evaluating the mobility and bioavailability of soil samples. The results of the sequential extractions of Cr, Cd, Ni, Zn, & Fe in the studied soil samples in Obunagha Community, Bayelsa State are presented in Table 1-5.

Chromium

Chromium is crucial for the metabolism of cholesterol, fat, and glucose. A deficiency can lead to hyperglycemia, increased body fat, and reduced sperm count, while elevated concentrations can be toxic and carcinogenic [9]. The concentration of Chromium in the distribution patterns investigated in the flooded and non-flooded farmlands based on their geochemical fractions are shown in Fig 1 and Table 1. The highest Chromium concentrations were found in FM1A (12.62 mg/kg) and FM2A (9.51 ± 2.02 mg/kg) within the water-soluble fraction (F1). Following this, the Exchangeable fraction ranged from 2.38 mg/kg to 7.34 mg/kg, the Carbonate fraction (F3) ranged from 2.00 mg/kg to 6.82 mg/kg, and the Organic carbon fraction (F5) ranged from 1.06 mg/kg to 6.63 mg/kg. Conversely, the Fe-Mn oxides and Reducible fractions exhibited the lowest concentrations. These results are inconsistent with the findings of Ajalaet *al.*, [10]. The WHO, [11](Table 7) sets the permissible limit for Chromium in soil at 0.05 mg/kg. Therefore, the concentrations of Chromium detected in all fractions could pose potential harm to human health. The high concentration of Chromium tends to oxidize to form Chromium (VI), which are the most toxic form of Cr. From the results it is observed that the flooded farmlands have highest Cr concentrations as compared to the non-flooded farmland.

Table 1: Concentration of Chromium in the different soil fractions

| Fraction | FMIA | FMIB | FMIC | FMID | FM2A | FM2B | FM2C | FM2D |
|----------------|----------------|----------------|----------------|----------------|---------------|---------------|---------------|---------------|
| Water Soluble | 12.62±3. 22 | 12.16±1. 54 | 10.83±0. 22 | 10.21±1. 10 | 9.51±2. 02 | 8.64±1. 36 | 8.43±0. 08 | 7.81±2. 90 |
| Exchangeable | 7.34±1.3 1 | 6.81±0.2 1 | 6.28±2.1 4 | 5.53±2.1 2 | 4.67±1. 54 | 3.84±0. 74 | 3.14±0. 66 | 2.38±1. 11 |
| Carbonate | 6.82±2.2 3 | 6.34±1.4 7 | 5.95±0.8 0 | 5.03±1.0 1 | 4.62±2. 09 | 4.10±1. 01 | 2.75±1. 21 | 2.00±0. 54 |
| Fe-Mn oxides | 3.82±1.0 2 | 3.52±0.2 1 | 2.94±1.1 1 | 2.52±0.0 1 | 3.45±0. 66 | 2.90±1. 77 | 2.35±0. 98 | 1.74±0. 22 |
| Organic carbon | 6.63±2.1 1 | 5.74±1.0 2 | 4.91±1.0 2 | 4.44±1.0 5 | 3.99±1. 02 | 2.80±0. 54 | 1.44±0. 77 | 1.06±0. 96 |
| Residual | 2.91±0.0 2 | 1.83±0.2 1 | 1.50±0.0 1 | 1.41±0.2 1 | 2.67±1. 36 | 2.36±0. 58 | 1.23±0. 97 | 1.05±0. 58 |

Cadmium

Cadmium, a heavy metal considered non-essential, poses significant toxicity even at minimal concentrations. Exposure can lead to learning disabilities and hyperactivity in children. The results of the sequential extraction of Cadmium in the soil samples of the flooded and non-flooded farmlands are shown in Table 2 and Figure 2. Cadmium was found to be associated mostly with the water-soluble fraction (F1) as 1.5mg/kg and 1.32mg/kg for farm1 and farm2 for 2mm deep flooded area respectively. This indicates that the Cadmium metals are mobilized. This is in agreement with the research findings of Osakwe, [4] which states that the appreciable amount of Cadmium was found in water soluble form and suggested that Cadmium to some extent is available in the soil because the metals in that fraction are usually for plant uptake. The next important fraction is the exchangeable fraction (F2) for farm 1 as 0.93mg/kg and farm 2 as 0.07mg/kg still on the 2mm deep flooded area. These signify the bioavailability of the cadmium metals in the study area. Generally, the concentrations of cadmium are relatively low in other fractions although they are still higher than WHO, [11] permissible limits (Table 7). It is also observed that the flooded farmlands have highest Cadmium concentrations as compared to the non-flooded farmland. The order of availability is: Water soluble (F1) > Exchangeable (F2) > Carbonate bound (F3) > Organic bound (F5) > Fe-Mn Oxides bound (F4) > Residue (F6).

Table 2: Concentration of Cadmium in the different soil fractions

| Fraction | FM1A | FM1B | FM1C | FM1D | FM2A | FM2B | FM2C | FM2D |
|----------------|---------------|---------------|---------------|---------------|-----------|---------------|---------------|---------------|
| Water Soluble | 1.50±0.0 1 | 1.35±0.2 1 | 0.91±0.0 2 | 0.91±0.0 2 | 1.30±0.02 | 1.15±0. 10 | 1.00±0.1 0 | 0.97±0.0 1 |
| Exchangeable | 0.93±0.0 9 | 0.82±0.0 2 | 0.75±0.0 3 | 0.07±0.0 3 | 0.07±0.01 | 0.07±0. 03 | 0.06±0.0 2 | 0.08±0.0 1 |
| Carbonate | 0.09±0.0 2 | 0.08±0.3 0 | 0.07±0.0 1 | 0.05±0.0 1 | 0.07±0.01 | 0.06±0. 04 | 0.05±0.0 1 | 0.05±0.0 3 |
| Fe-Mn oxides | 0.06±0.0 1 | 0.05±0.0 1 | 0.05±0.0 2 | 0.04±0.0 3 | 0.04±0.01 | 0.04±0. 01 | 0.03±0.0 2 | 0.03±0.0 2 |
| Organic carbon | 0.07±0.0 1 | 0.03±0.0 2 | 0.06±0.0 1 | 0.06±0.0 2 | 0.04±0.03 | 0.4±0.0 1 | 0.03±0.0 2 | 0.01±0.0 1 |
| Residual | 0.05±0.0 2 | 0.04±0.0 2 | 0.01±0.0 2 | 0.02±0.0 2 | 0.03±0.01 | 0.1±0.0 1 | 0.01±0.0 1 | 0.01±0.0 1 |

Nickel

Nickel is essential in small quantities for the body, primarily concentrated in the pancreas, where it plays a crucial role in insulin production. A deficiency can lead to liver disorders [12]. Certain plants demonstrate uptake and accumulation of nickel. Although nickel is recognized as an essential trace element in animals, its functional significance has not been conclusively demonstrated. The concentration levels in the six fractions of the soil samples are presented in Table 3 and figure 3.

The highest concentrations of Nickel were observed in the water-soluble fraction (F1), with 10.54 mg/kg in FM1A and 7.01 mg/kg in FM2A. This was followed by the Exchangeable fraction (F2) with 5.90 mg/kg for FM1A and 6.92 mg/kg for FM2A, and the Carbonate fraction with 4.14 mg/kg for FM1A and 3.93 mg/kg for FM2A. In contrast, the Fe-Mn oxides, Organic Carbon, and Residual fractions exhibited moderate concentrations. The result showed that in all the fractions, Ni concentration is more than the permitted level (0.02mg/kg) set by WHO, [11] (Table 7). The result indicates that Nickel metals are mobile and this is in disparity with the researches made by Osakwe, [13] and Ajala *et al.*, [10] whose

concentration for Nickel are low compared to the above results. These depict the bioavailability of nickel in the study area for plant uptake. The distribution of these metals across sequentially extracted fractions proceeds in the following order: Water Soluble (F1) > Exchangeable (F2) > Carbonates (F3) > Fe-Mn oxides (F4) > Organic bound (F5) > Residual (F6).

Table 3: Concentration of Nickel in the different soil fractions

| Fraction | FMIA | FMIB | FMIC | FMID | FM2A | FM2B | FM2C | FM2D |
|----------------|----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Water Soluble | 10.54±3. 20 | 9.84±0. 11 | 9.02±0. 22 | 8.04±0. 22 | 7.01±1. 21 | 5.78±0. 54 | 4.51±0. 41 | 3.69±0. 21 |
| Exchangeable | 5.90±1.0 9 | 4.52±2. 12 | 3.87±0. 02 | 2.92±0. 21 | 6.92±2. 11 | 5.21±1. 21 | 4.59±1. 47 | 3.75±0. 21 |
| Carbonate | 4.14±0.5 0 | 2.47±0. 01 | 2.98±0. 80 | 2.31±0. 04 | 3.93±1. 78 | 3.52±1. 21 | 2.57±1. 37 | 1.91±1. 47 |
| Fe-Mn oxides | 1.13±0.0 4 | 1.03±1. 00 | 1.00±0. 12 | 0.96±0. 01 | 0.89±0. 09 | 0.80±0. 02 | 0.69±0. 01 | 0.63±0. 03 |
| Organic carbon | 0.91±0.0 2 | 0.86±0. 10 | 0.79±0. 11 | 0.71±0. 02 | 0.59±0. 21 | 0.54±0. 31 | 0.49±0. 01 | 0.44±0. 25 |
| Residual | 0.35±0.2 1 | 0.17±0. 01 | 0.14±0. 02 | 0.07±0. 01 | 0.05±0. 40 | 0.02±0. 01 | 0.02±0. 02 | 0.01±0. 01 |

Zinc

Table 4 and Figure4 shows the concentrations of the Zinc metals in farm 1 and farm 2 respectively. Zinc was mostly concentrated in the water-soluble fraction (4.57-8.44mg/kg), although a significant amount was also present in the Exchangeable fraction (F2) (2.18-6.03mg/kg) and moderate contribution in the Carbonate (1.89-3.42mg/kg) and Fe-Mn oxide fraction (0.94-3.37mg/kg) while organic fraction and Residual fractions have low concentrations. At these levels Zinc could be a health threat to the

environment because it is above the permissible limit set by WHO, [11](Table 7). The result obtained is in agreement with the studies of Muller *et al.*, [14]. The high bioavailability of Zinc results to high toxicity of the study area. The metals are available in this order: Water Soluble (F1)>Exchangeable (F2) > Carbonates (F3) > Fe-Mn Oxides (F4) >Organic bound (F5)> Residual (F6).

Table 4: Concentration of Zinc in the different soil fractions

| Fraction | FMIA | FMIB | FMIC | FMID | FM2A | FM2B | FM2C | FM2D |
|----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Water Soluble | 8.44±0.01 | 7.83±0.08 | 6.52±1.33 | 5.97±1.05 | 7.53±2.47 | 6.80±2.08 | 6.00±3.21 | 4.57±0.21 |
| Exchangeable | 6.00±1.45 | 5.21±1.30 | 4.33±0.54 | 3.06±0.55 | 6.03±1.54 | 5.64±0.21 | 5.02±0.04 | 2.18±2.78 |
| Carbonate | 3.42±0.07 | 2.90±0.09 | 2.90±0.07 | 1.89±0.05 | 3.35±0.21 | 2.80±1.47 | 2.13±1.47 | 2.13±0.01 |
| Fe-Mn oxides | 3.37±1.03 | 2.19±1.11 | 1.54±0.02 | 1.00±0.08 | 2.36±0.12 | 1.98±0.23 | 1.53±0.45 | 0.94±1.41 |
| Organic carbon | 1.19±0.41 | 1.09±0.01 | 1.00±0.08 | 0.89±0.05 | 1.35±0.21 | 0.97±0.05 | 0.76±0.06 | 0.68±0.22 |
| Residual | 0.81±0.42 | 0.73±0.2 | 0.62±0.32 | 0.42±0.02 | 0.51±0.31 | 0.49±0.24 | 0.42±0.07 | 0.25±0.14 |

Iron Concentrations

Fig 5 shows the concentrations of the Iron metals in farm 1 and farm 2 respectively. The Exchangeable fraction with iron content varying from 5.35-10.52mg/kg, constituted the primary form of iron in all the soil samples. The next predominant fraction is seen at the water-soluble fraction (F1) of farm 1 as 9.52mg/kg. These results are not consistent with Ajala *et al.*, [10] whose results showed that Iron is not soluble in his study area which was Eke-Mgbo Afikpo area of Ebonyi state, South East of Nigeria. The present results show that Iron is soluble. The Residual fraction (F6) is the least fraction. Metals present in

residual forms are accessible to biota. The distribution of iron among the fractions follows the order Exchangeable (F2) > Water Soluble (F1) > Carbonates bound (F3) > Fe-Mn Oxides (F4) > Organic bound (F5) > Residual (F6).

Table 5: Concentration of Iron in the different soil fractions

| Fraction | FMIA | FMIB | FMIC | FMID | FM2A | FM2B | FM2C | FM2D |
|----------------|---------------|---------------|---------------|---------------|----------------|----------------|---------------|---------------|
| Water Soluble | 9.52±0. 22 | 8.88±0. 11 | 7.42±0. 02 | 7.02±0. 21 | 8.64±0.2 1 | 8.18±0.2 49 | 7.89±0. 21 | 6.86±0. 02 |
| Exchangeable | 8.25±2. 11 | 8.02±0. 14 | 7.85±0. 41 | 6.42±0. 21 | 10.52±2. 78 | 9.57±1.2 1 | 5.35±0. 25 | 6.89±0.4 1 |
| Carbonate | 9.44±1. 55 | 8.70±2. 23 | 7.08±2. 00 | 6.19±1. 36 | 8.72±1.0 0 | 8.00±2.7 8 | 6.92±0. 58 | 6.92±0. 47 |
| Fe-Mn oxides | 7.63± 12 | 7.02± 32 | 5.64± 54 | 4.90± 11 | 6.84±2.3 3 | 6.21±1.4 7 | 5.35±0. 25 | 4.22±0. 87 |
| Organic carbon | 7.14±0. 12 | 5.95±1. 32 | 4.54±1. 54 | 3.85±0. 11 | 5.92±0.2 8 | 5.92±2.4 3 | 4.38±2. 66 | 3.16±0. 36 |
| Residual | 4.81±2. 01 | 4.25±2. 02 | 3.74±1. 02 | 2.80±1. 54 | 3.97±1.1 3 | 3.13±1.1 1 | 2.90±1. 68 | 2.51±0. 01 |

3.2 Bioavailability

A sequential extraction technique was employed to assess the bioavailability of heavy metals within the study site. The bioavailability factor was calculated as the ratio of a metal's available concentration in soil to its total concentration. This factor indicates the capacity of a specific metal within the soil matrix to leach into the soil solution, facilitating absorption by plants. The basic indicator of the toxicity of a substance is its bioavailability [15]. The total and bioavailable concentration of heavy metals is presented in Table 6. The investigation showed a high bioavailability of metals in the flooded and non-flooded area of both farmlands. From the study, it shows that Cd (92.11-83.51%) with the highest % bioavailability is

potentially more bioavailable to the environment than the other metals studied. The overall order of mobility and bioavailability of the metals is Cd>Ni>Zn>Cr > Fe.

Table 6: %Bioavailability data for Farm 1 and Farm 2

| %Bioavailability data | | | | | |
|------------------------------|-----------|-----------|-----------|-----------|-----------|
| FARM 1 | | | | | |
| | Cr | Cd | Ni | Zn | Fe |
| A | 49.73 | 90.00 | 71.57 | 62.16 | 37.98 |
| B | 52.12 | 91.56 | 72.20 | 65.36 | 39.47 |
| C | 52.79 | 89.73 | 72.42 | 66.48 | 42.10 |
| D | 54.02 | 83.51 | 73.37 | 68.15 | 43.20 |
| FARM 2 | | | | | |
| A | 49.05 | 88.39 | 71.84 | 64.17 | 42.95 |
| B | 50.65 | 89.05 | 69.25 | 66.60 | 43.28 |
| C | 59.82 | 89.83 | 70.71 | 69.48 | 45.78 |
| D | 63.53 | 92.11 | 71.28 | 62.91 | 44.99 |

Table 7: World Health Organization Standards

| S/N | Metals | Highest Desirable (mg/kg) | Maximum Desirable (mg/kg) |
|------------|---------------|--------------------------------------|--------------------------------------|
| 1 | Fe | 1.0 | 3.0 |
| 2 | Zn | 1.0 | 3.0 |
| 3 | Cr | 0.05 | 0.05 |
| 4 | Cd | 0.003 | 0.003 |
| 5 | Ni | 0.01 | 0.02 |

Conclusion

From the findings of the research, it can be concluded that the concentration of the metals found in the flooded area were seen to be higher than that of the non-flooded area of the study. And also, the

concentrations of the metals were seen to be higher than World Health Organization (WHO) Permissible limits for a medium. This could be linked to various industrialization activities, flooding etc. which contributes to the metal's concentration increase. This significantly indicates that the metals pose a great environmental risk to the immediate community and environs. We therefore, recommend regular monitoring of the soils to mitigate the accumulation of these hazardous heavy metals.

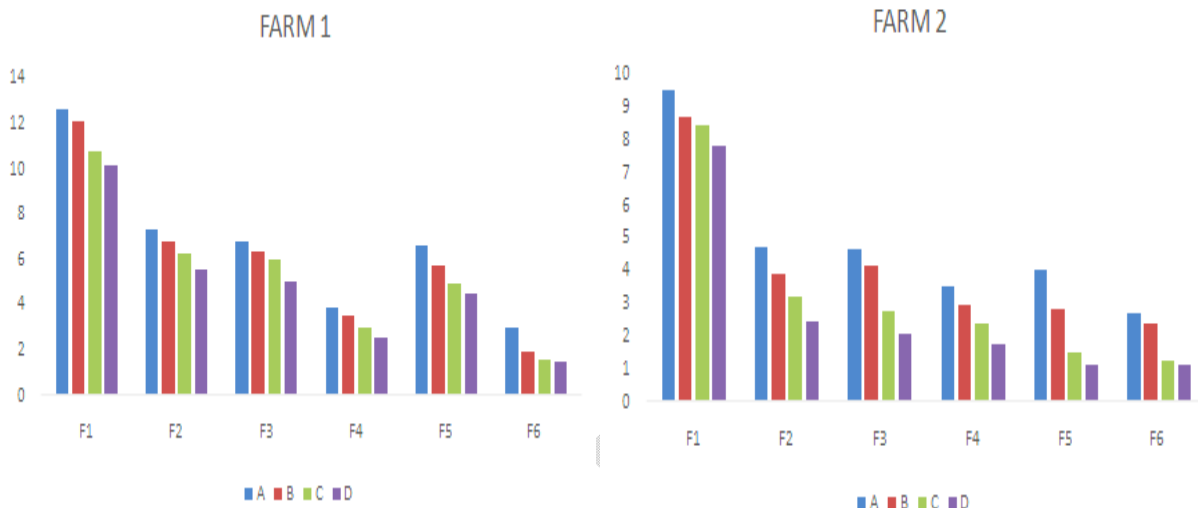


Fig 3: Concentration of Chromium. A = 3 mm-deep dry sediment [flooded area]; B = 30 cm deep; not including dry sediment [flooded area] C = 3 mm-deep surface soil [non-flooded area]; D = 30 cm deep; not including surface soil [non-flooded area]. Y-axis = concentration of metal in mg/kg

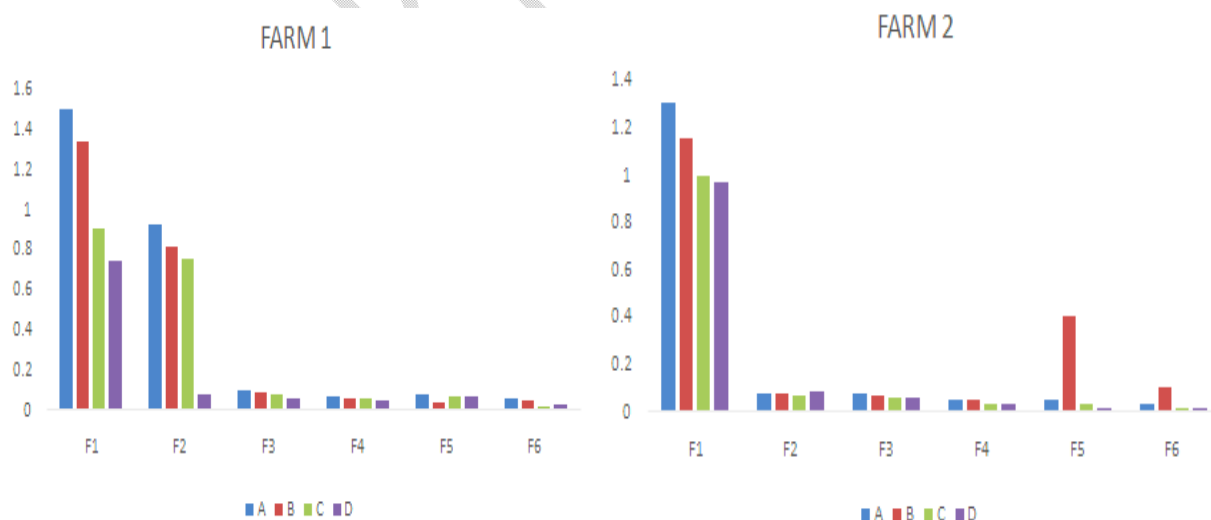


Fig 4: Concentration of Cadmium. A = 3 mm-deep dry sediment [flooded area]; B = 30 cm deep; not including dry sediment [flooded area] C = 3 mm-deep surface soil [non-flooded area]; D =

30 cm deep; not including surface soil [non-flooded area]. Y-axis = concentration of metal in mg/kg

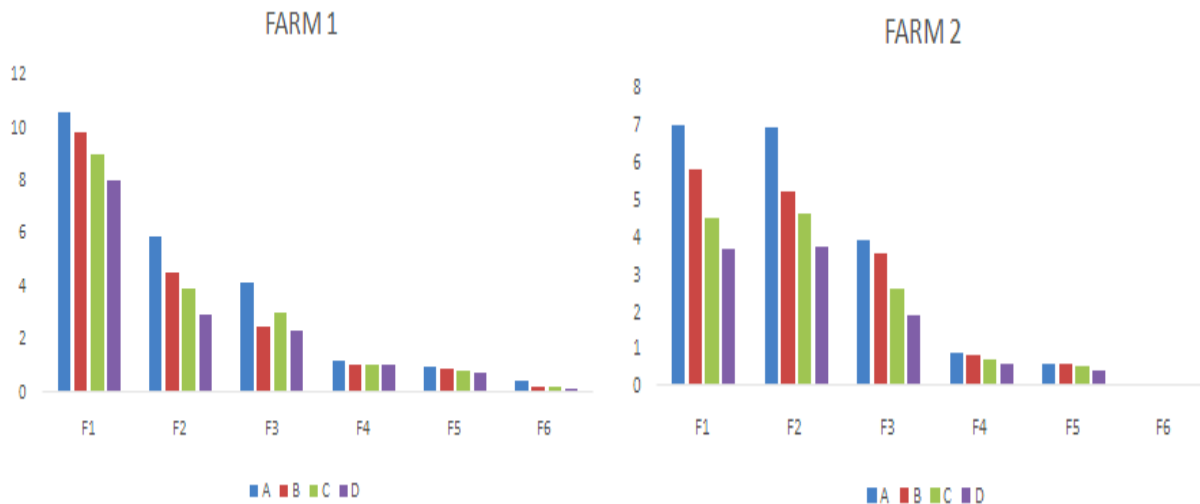


Fig 5:Concentration of Nickel. A = 3 mm-deep dry sediment [flooded area]; B = 30 cm deep; not including dry sediment [flooded area] C = 3 mm-deep surface soil [non-flooded area]; D = 30 cm deep; not including surface soil [non-flooded area]. Y-axis = concentration of metal in mg/kg.

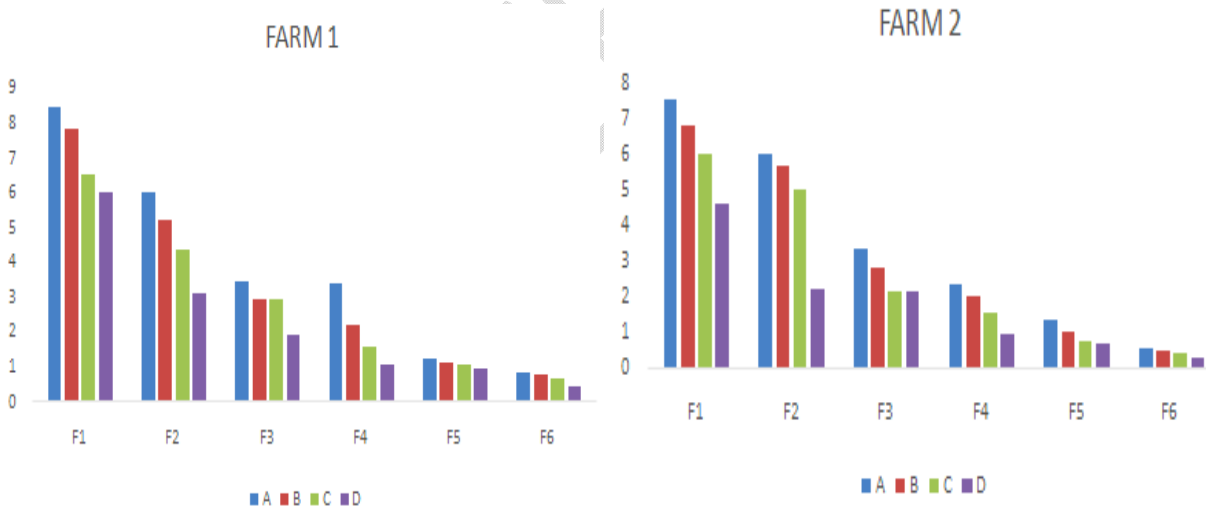


Fig 6:Concentration of Zinc. A = 3 mm-deep dry sediment [flooded area]; B = 30 cm deep; not including dry sediment [flooded area] C = 3 mm-deep surface soil [non-flooded area]; D = 30 cm deep; not including surface soil [non-flooded area]. Y-axis = concentration of metal in mg/kg.

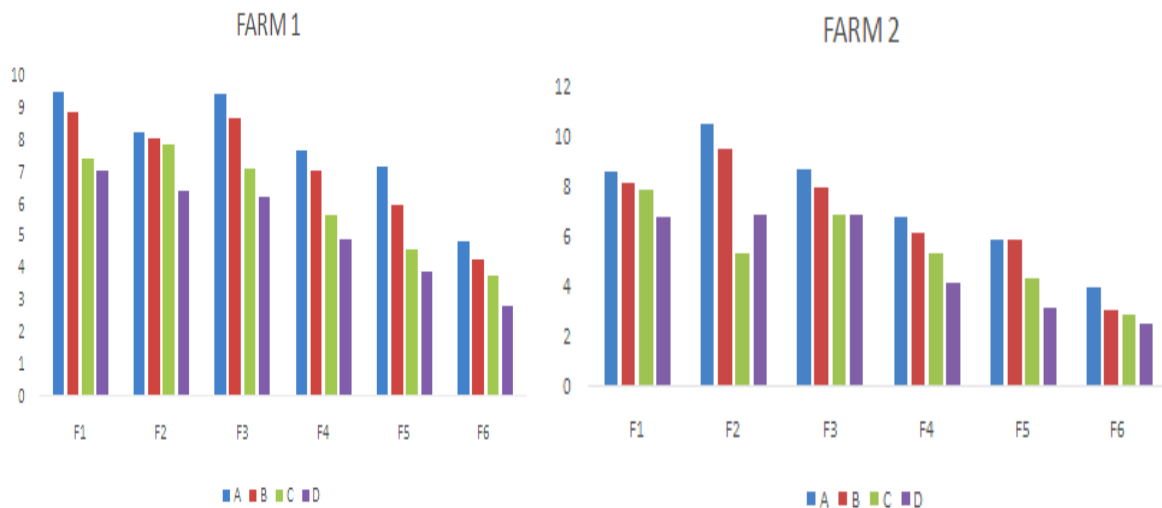


Fig 7:Concentration of iron. A = 3 mm-deep dry sediment [flooded area]; B = 30 cm deep; not including dry sediment [flooded area] C = 3 mm-deep surface soil [non-flooded area]; D = 30 cm deep; not including surface soil [non-flooded area]. Y-axis = concentration of metal in mg/kg.

Disclaimer (Artificial intelligence)

Option 1:

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

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Author(s) hereby declare that generative AI technologies such as Large Language Models, etc have been used during writing or editing of manuscripts. This explanation will include the name, version, model, and source of the generative AI technology and as well as all input prompts provided to the generative AI technology

Details of the AI usage are given below:

1.ChatGPT was used to paraphrase some sections of the manuscript with a view to improving clarity of language and readability of the manuscript.

2.

3.

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