

# Sequential Extraction of Heavy Metals from Soil Samples Collected from Selected Cocoa Farmland in Erijiyan, Ekiti State, Nigeria

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**Abstract-**Heavy metal pollution is of great concern due to their potential harmful effects on man and the environment, as soil and sediment are their primary repositories. Anthropogenic activities such as agricultural practices, industrial activities, and waste disposal have contributed to increases in heavy metal concentrations in soil. It is important to determine the effect of agricultural input on the heavy metal concentrations, mobility and bioavailability on cocoa farms by analyzing soil samples collected from selected locations to determine pH, content of organic matter, presence of water-soluble heavy metals and sequential extraction of heavy metals using standard analytical procedures. Results indicate random variation in the pH and organic matter content of soil with average values of  $6.49 \pm 0.12$  and  $2.30 \pm 0.11\%$ , respectively. The acid digestion of heavy metals was relatively higher than water-soluble heavy metals with the following mean values: Zn ( $33.70 > 11.30$ ), Fe ( $111.71 > 4.58$ ), Mn ( $1.84 > 1.24$ ), Cd ( $2.16 > 0.95$ ) and Co ( $1.66 > 1.01$ ). However, sequential extraction revealed that the heavy metals were distributed in all extractive steps, with the non-residual phase dominating and resulting in possible mobility and bioavailability of those heavy metals.

**Keywords-** Sequential Extraction; Heavy Metals; Cocoa; Farms

## I. INTRODUCTION

Soils are the primary repository for many harmful components, both chemical and biological, including heavy metals [1]. Much concern has been focused on the investigation of the total metal content of soil, with speciation (bioavailability) of these metals one of the useful tools of analysis [2-4]. Interestingly, sequential extraction of heavy metals is applicable to agriculture in term of identification, quantification and the extractible portion of biologically extractible heavy metals [5].

Metals in the soil can be enriched by both human (anthropogenic) and natural (lithogenic) factors, such as weathering, earthquake and environmental pollution, among others. However, it is important to properly identify the geochemical phases in which metals may be bound, as heavy metal mobility within soil differs from native to anthropogenic [6, 7]. Heavy metals may be distributed in soil components as exchangeable, adsorbed on soil organic matter, precipitated or complexed [4]. In terms of bioavailability, various species of metals (e.g., Cu, Co, Ni and Zn) are more biologically available than others [3, 8]. If bioavailability is related to the mobility of heavy metals, then higher concentrations of mobile toxic metals in the soil column increases the potential for plant uptake as well as leaching into environmental soil and water bodies, and their eventual presence in man.

Agricultural inputs such as fertilizers, pesticides, bio-solids and manures have contributed increasing levels of essential and toxic metals in soil [9-11]. As a result, there is a need for periodic and constant monitoring of the distribution of such metals in agricultural soil. The aim of the research is to determine the effect of agricultural input on the distribution of heavy metals in various phases of soil, in order to examine their bioavailability and mobility.

## II. METHODOLOGY

### A. Study Area

Bulk soil samples were collected from a cocoa farm in Erinjiyan Ekiti in southwestern Nigeria, located 30 km northwest of Ado Ekiti and 50 km from Ile-Ife at latitude  $7.35^{\circ}$  N and longitude  $5.05^{\circ}$  E, and approximately 350 meters above sea level. Erinjiyan enjoys a tropical climate with two distinct seasons: the rainy season (April to October) and dry season (November to March). The temperature ranges from  $20^{\circ}$  –  $36^{\circ}$ C with high humidity.

### B. Sample Collection, Preparation and Analysis

Eight soil samples were randomly collected for analysis of source and mobility of heavy metals at a cocoa farm using a calibrated soil auger, and were immediately placed in sealed polythene bags. The samples were collected at depths from 0 – 15 cm, from eight points at 40 m intervals from the first sample location. The samples were air-dried, ground up and sieved with 4 mm mesh. Each sample was immediately placed in a leached polythene bag and tightly sealed. The pH and organic matter content of soil samples were immediately determined using standard analytical procedures as prescribed by AOAC [12].

### C. Water Soluble

The determination of the availability of water-soluble metals in the soil samples were measured by dissolving 1g of an air-dried and homogenized soil sample, weighed in a centrifuge tube, before adding 10 mL of deionised water. The centrifuge tube was then operated for three hours. The resulting solution was diluted to 25 mL and analyzed for heavy metals by Atomic Absorption Spectrophotometry (model PG 990).

### D. Acid Digestion

The air-dried and homogenized soil samples of 0.1g were treated with a mixture of 30 mL HNO<sub>3</sub>, 10 mL HClO<sub>4</sub> and 30 mL of HF, and placed in a microwave oven for four minutes. The samples were then filtered into a volumetric flask and diluted to 100 mL with distilled/deionized water. The resulting solutions were analyzed for heavy metals concentrations by Atomic Absorption Spectrophotometry (model PG 990).

### E. Sequential Extraction Procedures

The distribution of heavy metals in various phases of the solids was conducted as prescribed by Tessier et al. [13], according to the following steps:

- 1). Metals in the aqueous phase of soil were extracted with 45 mL of 1M ammonium acetate (pH=5) with acetic acid by stirring for 24 hours;
- 2). Metals in the exchangeable phase were determined by extraction with 22.5 mL hydroxylammonium chloride (1M) and 22.5 mL acetic acid (25%), with stirring at room temperature;
- 3). Metals adsorbed on inorganic soil constituents were extracted by 12.5 mL of HCl and stirring for 24 hours;
- 4). Metals adsorbed on organic matter were treated with 12.5 mL of 0.5 NaOH and stirred for 24 hours; the solution was later dried under an IR lamp at 60°C and then digested in a microwave oven with 4 mL of 65% HNO<sub>3</sub> and 2 mL of 40% HF;
- 5). Metals precipitated as pure or mixed solids were extracted using 12.5 mL of 8M HNO<sub>3</sub> and digested for three hours at 80°C;
- 6). Metals in the residual phase of soil were digested with 4 mL of oxidising mixture (HNO<sub>3</sub>: HCl) and 6 mL of HF in a Teflon recipient, and placed in a microwave oven. Heavy metal concentrations were determined in all steps by Atomic Absorption Spectrophotometry (model PG 990).

### F. Data Analysis

All data collected were replicates of three determinations; statistical analyses were conducted by calculating the mean, standard deviation, coefficient of variation and bar charts.

## III. RESULTS AND DISCUSSION

### A. Physicochemical Parameter

The result of the pH and organic matter content (OMC) of soil samples collected from selected locations on a cocoa farm located at Erijiyan, Ekiti State are shown in Table 1.

TABLE 1 THE pH AND ORGANIC MATTER CONTENT (OMC) OF SELECTED LOCATIONS IN ERIJIYAN FARMS

Location/parameters	1	2	3	4	5	6	7	8	Mean
pH	6.20	6.20	6.10	6.30	6.90	6.68	6.70	6.80	6.49 ±0.12
OMC %	4.40	3.50	2.80	1.80	1.50	2.20	1.40	0.90	2.30 ±0.11

Results obtained from pH measurements revealed that the farms had pH values ranging from 6.10 – 6.90, with an average pH of 6.49 ±0.12. Moderately low pH values have been shown to enhance bioavailability, solubility and the possible leaching of heavy metals [6, 14]. However, some heavy metals such as Zn, Fe, and Mn play a beneficial role in plant growth and development at low concentrations.

The organic matter content of soil samples ranged from 0.90 – 4.40%, with an average value of 2.30 ±0.11% at locations in the cocoa farms. Organic matter content is one factor which indicates vast arrays of carbon-containing compounds in the soil. This is typically created by the decay of plants, microbes and other organisms, such as decomposed wood, dead animals and organic wastes, which play vital roles in nutrient water and biological cycles. This also increases the water holding capacity of soil [15].

## B. Distribution of Heavy Metals in Different Phases of Soil

### 1) Metal Speciation

The ranges of heavy metal concentrations from water solubility and acid digestion tests are depicted in Table 2. Generally, obtained concentrations of heavy metals were comparatively higher according to acid digestion than those determined by solubility analysis. These include: soluble Zn (1.40 – 44.80; 1.10 – 15.10), Fe (42.80 – 216.70; 2.8 – 9.6), Mn (0.80 – 2.60; 0.60 – 1.80), Cd (0.91 – 2.59; 0.60 – 1.50) and Co (0.90 – 219; 0.60 – 1.60), all measured in mg/kg. The higher concentrations determined by acid digestion could indicate that some heavy metals are available in soil in various complex forms, or that they may be bound to important soil constituents which may not easily be removed by ordinary water solubility experiments [16, 17].

The relative solubilities of these heavy metals in water indicated that considerable levels may have found their way into the food chain via bioaccumulation and leaching into surrounding water bodies. Awokunmi et al. [6] reported the possibility of the lateral flow of heavy metals as a result of leaching in a study of selected dumpsites in Ekiti State, Nigeria.

TABLE 2 CONCENTRATION OF HEAVY METALS IN WATER SOLUBLE AND ACID DIGESTION (MG/KG)

		WS	AD
Zn	Range	1.10 – 15.1	1.4 – 44.80
	Mean	11.30	33.70
	SD	4.55	1.01
	CV%	40.3	32.90
Fe	Range	2.8 – 9.6	42.80 – 216.7
	Mean	4.58	111.71
	SD	2.41	0.34
	CV%	52.60	20.00
Mn	Range	0.60 – 1.80	0.80 – 2.60
	Mean	1.24	1.84
	SD	0.44	0.23
	CV%	35.5	27.4
Cd	Range	0.60 – 1.50	0.91 – 2.59
	Mean	0.95	2.16
	SD	0.32	0.24
	CV%	33.7	20.7
Co	Range	0.60 – 1.60	0.91 – 2.19
	Mean	1.01	1.66
	SD	0.29	0.12
	CV%	28.7	11.3

WS = Water Soluble, AD = Acid Digestion, SD = Standard Deviation, CV = Coefficient of Variation.

### 2) Sequential Extraction of Heavy Metals

Soil samples collected from selected cocoa farms located in Erijiyan Ekiti, Nigeria were subjected to sequential extraction procedures as prescribed by Tessier et al. [13], in order to determine the distribution and mobility of heavy metals within the soil profile. The five heavy metals considered in this study are Zn, Fe, Mn, Cd and Co. From the results presented in Figs. 1-5, all heavy metals were found in all extractive steps. The concentrations of these metals vary from exchangeable, carbonate bound, complexed to Fe–Mn, and bound to organic matter.

Metals bound to the non-residual phases of soil have been reported to be a result of anthropogenic input [18]. It has been previously reported by Awokunmi et al. [3] that the most mobile phase of heavy metals in Tessier's procedures are present in the exchangeable phase of soil. Since mobility is directly related to bioavailability [17], most of these heavy metals may be bio-available to the cocoa plant, and thus may eventually find their way into the food chain.

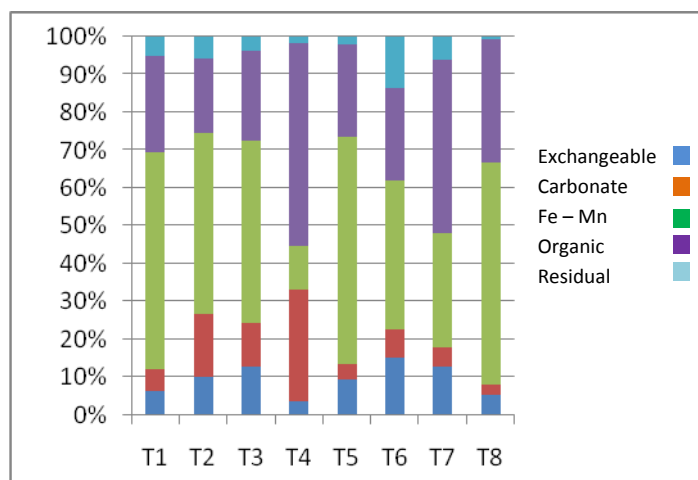


Fig. 1 Percentage distribution of Zn in the five extracted phases

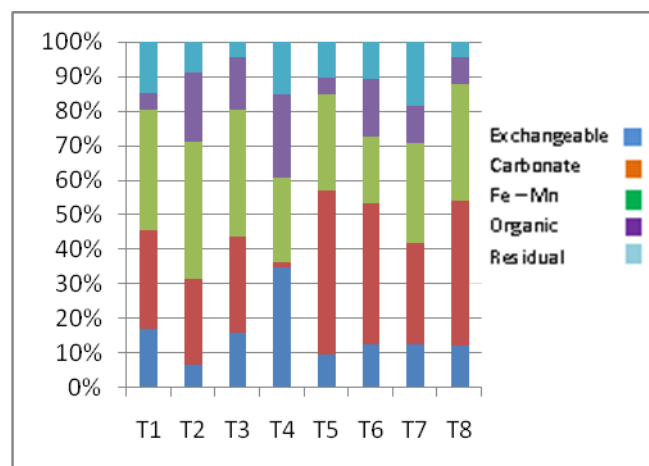


Fig. 2 Percentage distribution of Fe in the five extracted phases

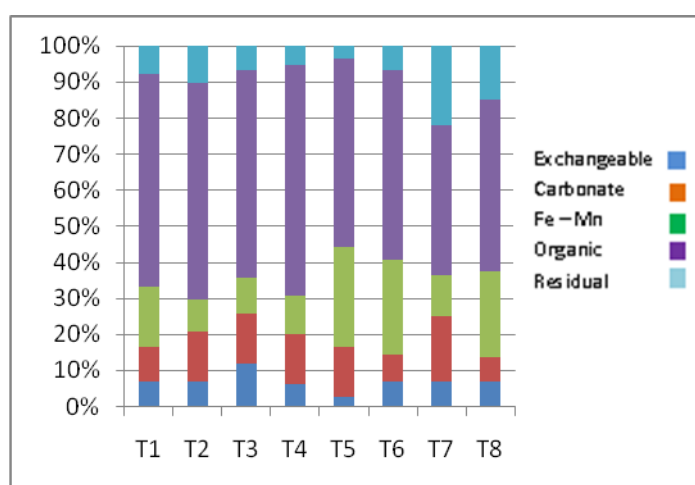


Fig. 3 Percentage distribution of Mn in the five extracted phase

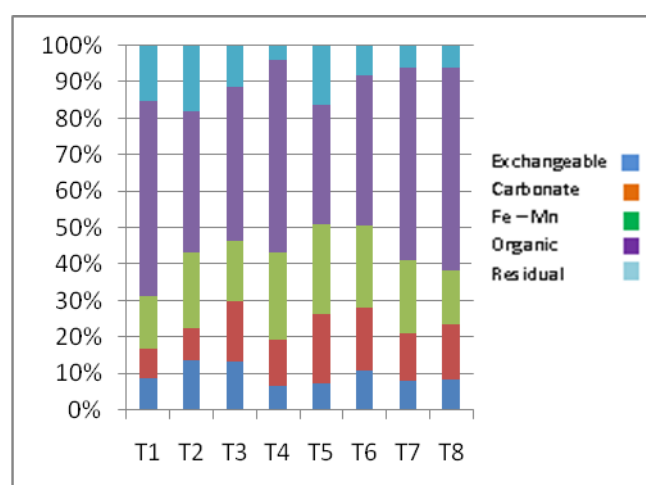


Fig. 4 Percentage distribution of Cd in the five extracted phases

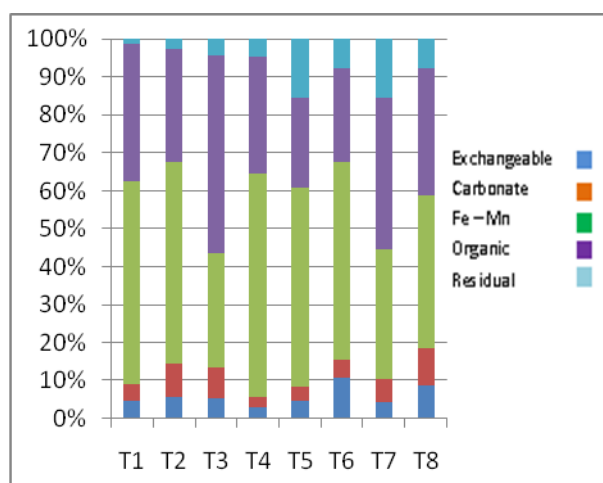


Fig. 5 Percentage distribution of Co in the five extracted phases

#### IV. CONCLUSION

The assessment of soil collected from the study area revealed that most of the studied heavy metals were found in appreciable concentrations as water soluble, which was further indicated as a result of higher levels of exchangeable fractions as demonstrated by sequential extraction procedures. However, there is the possibility of mobility and bioavailability of these metals and subsequent uptake by the cocoa plant, which may eventually allow their entrance into the food chain.

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