



## Assessment of Some Heavy Metals and Physiochemical Parameters of Soil Samples from Biu, Biu Local Government Area, Borno State, Nigeria

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### ABSTRACT

Biu is central to the known Biu province which harbors mostly the Pabirs and Buras who considered farming not only as a source of livelihood but as a pride. Cereal and other agricultural products are produced for both commercial and consumption purposes, thus, a lot of agrochemicals and other soil amendments are employed to improve harvest. Also, the soil of the area is mostly found either amongst or surrounded by mountains or rocky environment, thus the need to assess level of some heavy metals and physicochemical parameters of the soil samples is critical. Atomic Absorption Spectrophotometer (AA-6800 SCHIMADZO) was used to determine the concentration of the heavy metals in the soil. Determinations of pH, electrical conductivity, cation exchange capacity (CEC) organic carbon, organic matter, calcium, sodium and potassium were carried out using standard methods. The results revealed the concentrations of Mn ranging between 6.45 and 16.98 mg/kg; 5.34 and 14.324 mg/kg Fe; 0.98 and 1.67 mg/kg Ni; 0.19 and 0.916 mg/kg Co; 0.43 and 0.838 mg/kg Cu; 0.326 and 1.269 mg/kg Zn; 0.012 and 0.435 mg/kg Pb; 0.043 and 0.813 mg/kg Cd and 0.02 and 0.80 mg/kg As. The levels of heavy metals in the sampled areas are in the following order Mn > Fe > Ni > Zn > Co > Cu > Cd > As > Pb. The predominant high concentrations of manganese and iron in all the depths for pre- and post harvests soil samples observed from the results could be associated to nature of soil of the area which is mostly found amongst or surrounded by mountains or scattered rocks. It is also clearly observed that the concentration of the heavy metals is higher in the post-harvest compared to pre-harvest, this could be attributed to the use of agrochemicals applied to boost harvest and to control pest. The levels of some physicochemical parameters in soil samples from different agricultural locations during pre-harvest and post-harvest revealed pH values ranging between 5.74 and 6.32; 28.0 and 151.0 ( $\mu\text{Scm}^{-1}$ ) electrical conductivity; 0.92 and 1.58 % organic carbon; 1.59 and 4.17 % organic matter; 6.21 and 90.9 c.mol/kg CEC; 1.40 and 37.0 mg/kg Ca; 0.12 and 0.26 mg/kg Na and 0.23 and 2.94 mg/kg K. The decrease in heavy metals concentration with increase in depth is in agreement with increase in pH with increase in depth. Low pH increases the solubility and mobility of heavy metals since the mobility and availability of heavy metals are considerably greater in acidic soils than in near neutral or alkaline soils. In this study organic carbon and organic matter are observed to decrease with depth both in the pre-harvest and post-harvest, high organic matter content helps in high retention capacity of many pollutants. The cation exchange capacity (CEC) is found to decrease in depth with rise in pH values. Levels of Na, Ca and K detected in the soil are within the safe limit set by FAO, however, the heavy metals were found to be above the limit.

**Keywords:** Agrochemicals, Cereal, Harvest, Heavy Metals, Physiochemical Properties

### INTRODUCTION

Soil being essential for growth of plants is endangered by so many factors, the most crucial being sources of heavy metals. Monitoring the endangerment of soil by heavy metals is of interest due to their influence on ground and surface water (Clemente *et al.*, 2008; Boukhalfa, 2007) and also on flora (Pandey and Pandey 2008; Stobrawa and Lorenc-plucińska, 2008), animals and humans (Devries *et al.*, 2007). The overall behavior of heavy metals in soil is said to be governed largely by their sorption and desorption reactions with different soil constituents, especially clay components (Appel and Ma, 2002). The chemical behavior of heavy metals in soils is controlled by a number of

processes, including metal cation release from contamination source materials (e.g., fertilizer, sludge, smelter dust, ammunition, slag), cation exchange and specific adsorption onto surfaces of minerals and soil organic matter, and precipitation of secondary minerals (Manceau *et al.*, 2000). The relative importance of these processes depends on soil composition and pH. In general, cation exchange reactions and complexation to organic matter are most important in acidic soils, while specific adsorption and precipitation become more important at near-neutral to alkaline pH values (Voegelin *et al.*, 2003).

Filep (1998) stated that contaminants reaching the soil can be divided into two groups,

namely micropollutants and macropollutants. Micropollutants are natural or anthropogenic molecules, which are toxic at very low concentration. Macropollutants are present in the environment locally and/or temporarily to a much

higher degree than normal level. Toxic heavy metals and micronutrients utilized as metal ions exist in the soil as species with several types of mobility (Table 1) and take part in many interactions.

**Table 1: Chemical species of heavy metals in soil with respect to solubility (filep, 1998)**

Species	Examples
Free metal ion	[Cd(aq)] <sup>2+</sup> , [Cu(aq)] <sup>2+</sup> , [Pb(aq)] <sup>2+</sup>
Ion pairs and inorganic complexes	PbCO <sub>3</sub> , PbHCO <sub>3</sub> <sup>+</sup> , PbCl <sup>+</sup> , CdCO <sub>3</sub> , CdCl <sup>+</sup>
Organic complexes	R{ <i>coo</i> }M; M-fulvic acid complexes
Metal sorbed to <i>inorganic colloids</i>	Exchangeable and nonexchangeable forms (in solid phase)
Metal sorbed to <i>organic colloids</i>	Exchangeable forms and M-humic acid complexes (in solid phase)
Precipitates	PbCO <sub>3</sub> , CdCO <sub>3</sub> , CdS etc. (in solid phase)

In liquid phase they exist as hydrated ions, soluble organic and inorganic complexes and as a component of fine disperse floating colloids.

In the solid phase they occur as insoluble precipitates and minerals, on the surface of organic and inorganic colloids in exchangeable and non-exchangeable (specific adsorbed) forms. Atanassov *et al.* (1999) stated that heavy metals are of interest due to their abundance in the environment, which has increased considerably as a result of human activities. Their fate in polluted soils is a subject of study because of the direct potential toxicity to biota and the indirect threat to human health via the contamination of groundwater and accumulation in food crops (Martinez and Motto, 2000). Heavy metals are dangerous because they tend to bioaccumulate. This means that the concentration of a chemical in a biological organism becomes higher relative to the environmental concentration (Kampa and Castanas, 2008). Heavy metal pollution of soil enhances plant uptake causing accumulation in plant tissues and eventual phytotoxicity and change of plant community (Gimmler *et al.*, 2002).

Soil organic matter (SOM) is the organic matter component of soil, consisting of plant and animal residues at various stages of decomposition, cells and tissues of soil organisms, and substances synthesized by soil organisms. SOM exerts numerous positive effects on soil physical and chemical properties, as well as the soil's capacity to provide regulatory ecosystem services (Brady and Weil, 2002). Particularly, the presence of SOM is regarded as being critical for soil function and soil quality. SOM also acts the major sink and source of soil carbon (C). Although the carbon (C) content of SOM is known to vary considerably (Périer and Ouimet, 2008; Jain *et al.*, 1997) SOM is typically estimated to contain 58% C, and the terms soil organic carbon (SOC) and SOM are often used interchangeably, with measured SOC content often serving as a proxy for SOM. Soil represents one of the largest C sinks on the planet and plays a major

role in the global carbon cycle. Therefore, SOM/SOC dynamics and the capacity of soils to provide the ecosystem service of carbon sequestration through SOM management have received considerable attention in recent years. The concentration of SOM in soils generally ranges from 1% to 6% of the total topsoil mass for most upland soils. Soils whose upper horizons consist of less than 1% organic matter are mostly limited to desert areas, while the SOM content of soils in low-lying, wet areas can be as high as 90%. Soils containing 12-18% SOC are generally classified as organic soils (Troeh and Louis, 2005).

For investigating the heavy metals in soils Wu *et al.* (2007) found that the inter correlation between heavy metals and active soil components (such as iron oxides, organic matter, and clay) is the major predictive mechanism and they concluded that the correlation with total Fe (including active and residual Fe) is the major mechanism. In a study conducted by Chen *et al.* (1999) it was suggested that concentrations of most trace metals in Florida soils are primarily controlled by soil properties, clay, organic carbon content, and CEC showed significant correlation with concentrations of most trace metals where the soil pH had significant positive correlation with concentrations of As, Cd, Cr, Cu, Mn, Se, and Zn. Adsorption of metal cations has been correlated with such soil properties as pH, redox potential, clay, soil organic matter, Fe and Mn oxides, and calcium carbonate content (McLean and Bledsoe, 1992). Heavy metal dynamics in soils are complex and influenced by numerous factors such as the pH, soil organic matter, soil texture, redox potential, and temperature (Alloway and Jackson, 1991). Also, high calcium concentration in the treated soils can significantly hinder the metal transport, because the migration and precipitation of calcium as bicarbonates and hydroxides can clog soil pores and increase the soil buffer capacity, constraining the advance of the acid front (De-Gioannis *et al.*, 2007).

The link between soil pH and heavy metal threshold values reflects the complex interaction between heavy metals and the various soil properties (Gawlik and Bidoglio, 2006). pH is a measure of the hydrogen ion concentration acidity or alkalinity of the soil. Measured on a logarithmic scale, a soil at pH 4 is 10 times more acidic than a soil at pH 5 and 100 times more acidic than a soil at pH 6. Alkalinity is usually an inherent characteristic of soils, although irrigation can increase the alkalinity of saline soils. Soils made alkaline by calcium carbonate alone rarely have pH values above 8.5 and are termed 'calcareous'. Under normal conditions, the most desirable pH range for mineral soil is 6.0 to 7.0 and 5.0 to 5.5 for organic soil. The buffer pH is a value used for determining the amount of lime to apply on acidic soils with a pH less than 6.6. Increases in soil pH can occur as the result of organic matter decomposition, because mineralization and ammonification processes release OH<sup>-</sup> ions and consume H<sup>+</sup> ions (Ritchie and Dolling, 1985). Colloid and metal mobility, was enhanced by decreases in solution pH and colloid size, and increases in organic matter, which resulted in higher elution of sorbed and soluble metal loads through metal-organic complex formation (Karathanasis *et al.*, 2005).

The objectives of the study are to determine the concentrations of some heavy metals such as arsenic (As), cadmium (Cd), cobalt(Co), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) zinc (Zn), pH, electrical conductivity (EC) organic carbon percentage, organic matter percentage, cation exchange capacity(CEC) and also, some macro nutrients which include K<sup>+</sup>, Ca<sup>+</sup>, Na<sup>+</sup> in soil samples in some agricultural locations in Biu from Biu local government area.

## Materials and Methods

### Sampling collection points

The soil samples were collected from different farm lands in Biu town. Soil samples were collected at a depth of 0-5cm, 5-10cm and 10-20cm, using spiral auger in a clean polythene bags for both pre- and post-harvest. Soil samples were collected three times monthly for two seasons, before plantation and after harvesting to signify pre- and post-harvest respectively. All samples were labelled appropriately, stored in cool container and transported to Chemistry Department Laboratory, University of Maiduguri for further analysis. Soil samples from the agricultural locations were collected three times a month for a period of two years.

### Soil Sample Preparation

The soil samples were oven dried at 105°C for 24 h, followed by grinding and sieving using 0.18 mm sieve. A 0.5 g of dry soil sample was poured into a graduated test tube and mix with

2 ml of aqua regia 1:3 (1 conc. HCl: 3 conc. HNO<sub>3</sub>). The mixture was digested on a hot plate at 95°C for 1 h and allowed to cool to room temperature. The sample was then diluted to 10 ml using distilled water and left to settle overnight. The supernatant was filtered prior to analysis using AAS as specified in Adam, (1991).

### Determination of pH and EC in Soil Samples

Ten grams (10g) of soil sample was weighed into a 50ml beaker and 25ml of distilled water was added. The suspension was allowed to stand for one hour with occasional stirring using a glass-rod (stirrer). The pH meter was calibrated using buffer solutions of pH 4 and pH 7.0, before immersing the electrode into the supernatant of the suspension. The reading was taken when it was fairly stable without further stirring. The reading was then recorded as "soil pH measured in 1:2.5 soil water ratios". The electrolytes of the pH meter were rinsed with distilled water and wiped dry with a clean tissue before immersing in distilled water prior to each subsequent measurement. The suspension was then taken in the same manner with the use of an EC meter. The results were recorded in mScm<sup>-1</sup>.

### Determination of Exchangeable Cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) in Soil

Ten grams (10g) of air dried soil sample was weighed into a 150ml plastic bottle and 30ml of 1N NH<sub>4</sub>OAC (pH 7.0) was added and shaken for 2hours. The extract was filtered into a clean 100ml volumetric flask, 30ml of 1N NH<sub>4</sub>OAC was again added to the residue and shaken for 30 minutes, it was then filtered into the same volumetric flask. Another 30ml of 1N NH<sub>4</sub>OAC was added and shaken for 30 minutes which was filtered into the same volumetric flask. The extract was made up to 100ml with the extracting solution (Doll and Lukas, 1973).

### Titrimetric Determination of Ca<sup>2+</sup> and Mg<sup>2+</sup> in Soil

Ten milliliters (10ml) of the extract above was transferred into a clean 250ml conical flask and 100ml of distilled water was added. Furthermore, 15mls of NH<sub>4</sub> buffer, 10 drops each of KCN, NH<sub>2</sub>OH.HCl, K<sub>4</sub>Fe (CN)<sub>6</sub> and TCA were also added. Few minutes was allowed for the reaction to take place after which 5 drops of EBT indicator were added and the solution was titrated with 0.01N Na<sub>2</sub> EDTA to a permanent blue colour (Doll and Lukas, 1973).

Calculations;

$$\text{Meq Ca}^{2+}/100\text{g soil} = \frac{a \times TCa \times 100 \times 1000}{W \times V2 \times \text{eq.wt of Ca}}$$

$$\text{Meq Mg}^{2+}/100\text{g soil} = \frac{a \times TMg \times 100 \times 1000}{W \times V2 \times \text{eq.wt of Mg}}$$

Where

a = mls of 0.01N EDTA used for titration of sample

TCa = titration factors of EDTA against Ca i.e.

$$\frac{0.01 \times 40.08}{1000} = 0.0004008$$

TMg =

$$\text{titration factors of EDTA against Mg } \frac{0.01 \times 24.32}{1000} = 0.0002432$$

V<sub>1</sub> = total volume of extract

V<sub>2</sub> = mls of aliquot or filtrate

W = weight of sample used

#### Determination of Sodium and Potassium in Soil

The determination was by flame photometric methods, and the concentration of potassium and sodium (in ppm) of each was directly found from the standard curve. The amount of potassium in the sample (Meq) was calculated using the following formulae (Doll and Lukas, 1973).

Calculation

$$\text{Meq } K^+ / 100\text{g soil} = \frac{\text{ppm from graph} \times d.f \times 100 \times V}{1000 \times w \times \text{eq. Wt of } K^+}$$

$$\text{Meq } Na^+ / 100\text{g soil} = \frac{\text{ppm from graph} \times d.f \times 100 \times V}{1000 \times w \times \text{eq. Wt of } Na^+}$$

Where

w = weight of sample df = dilution factor V = (100) total volume of sample made

#### Determination of Organic Carbon (wet oxidation method by Walkey Black)

The % O.C was determined by wet oxidation method. 1g of air-dried (passed through 0.5mm sieve) soil sample was weighed into a 250ml conical flask. 10ml of 1N potassium dichromate was added with the help of clean pipette. Using a clean measuring cylinder, 20ml of

concentrated sulphuric acid was added. After cooling, 100ml of distilled water was added followed by 10ml of ortho-phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 0.2g of sodium fluoride (NaF). 5 drops of diphenylamine indicator was added which turned the colour to deep violet (Walkey and Black, 1934). The excess chromic acid was then titrated with 0.5N ferrous sulphate (N FeSO<sub>4</sub>). The endpoint was recorded as the colour changed from deep violet to deep green. The same procedure was repeated on the blank (without soil sample). The amount of soil sample was recorded and the strength of the FeSO<sub>4</sub> was titrated and finally the % O.C oxidized by potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) was calculated using the formulae below

$$\% \text{ O.C } = \frac{B - T \times F \times 0.39}{W}$$

Where

B = amount of 0.5N FeSO<sub>4</sub> solution required in blank titration

T = amount of 0.5N FeSO<sub>4</sub> solution required in the titration of sample

F = Normality of FeSO<sub>4</sub> and W = weight of soil sample

#### RESULTS

The concentrations of heavy metals in soil samples from 0-5, 5-10 and 10-20cm depth in Biu from local government area during pre and post-harvest are as presented in Table 2 (Figure 1). The concentrations of Mn ranged between 6.45 and 16.98 mg/kg; 5.34 and 14.324 mg/kg Fe; 0.98 and 1.67 mg/kg Ni; 0.19 and 0.916 mg/kg Co; 0.43 and 0.838 mg/kg Cu; 0.326 and 1.269 mg/kg Zn; 0.012 and 0.435 mg/kg Pb; 0.043 and 0.813mg/kg Cd and 0.02 and 0.80 mg/kg As. The levels of heavy metals in Biu locations are in the following order Mn > Fe > Ni > Zn > Co > Cu > Cd > As > Pb.

**Table 2: Mean Concentrations of Some Heavy Metals in Different Sampling Depth in Biu**

			Mn	Fe	Ni	Co	Cu	Zn	Pb	Cd	As
		0-5cm	10.837	10.57	1.378	0.916	0.838	1.269	0.435	0.26	0.02
		5-10cm	8.907	9.524	1.238	0.359	0.711	0.793	0.424	0.231	0.021
Pre-Harvest	Biu	10-20cm	6.45	5.34	0.98	0.31	0.43	0.55	0.34	0.16	0.016
		0-5cm	16.98	14.175	1.67	0.245	0.777	0.552	0.059	0.813	0.29
		5-10cm	15.34	14.66	1.45	0.208	0.732	0.532	0.026	0.678	0.5
Post-Harvest	Biu	10-20cm	11.23	14.324	1.09	0.19	0.65	0.326	0.012	0.043	0.8

The levels of some physicochemical parameters in soil samples from different agricultural locations in Biu from Biu local government area during pre-harvest and post-harvest are as presented in Table 3. pH ranged between 5.74 and 6.32; conductivity ranged between 28.0 and 151.0(μScm<sup>-1</sup>), while organic

carbon varies between 0.92 and 1.58 %; organic matter ranged between 1.59 and 4.17 %, CEC varies between 6.21 and 90.9 C.mol/Kg; Ca varies between 1.40 and 37.0 mg/kg; Na ranged between 0.120 and 0.26 mg/kg and K ranged between 0.23 and 2.94 mg/kg.

**Table 3: Physicochemical Parameters in Soil Samples from Different Agricultural Locations in Biu During Pre-Harvest and Post-Harvest**

			pH	Conductivity ( $\mu\text{Scm}^{-1}$ )	Organic Carbon (%)	Organic Matter (%)	CEC C.mol/Kg	Ca Mg/kg	Na Mg/kg	K Mg/kg
Pre-Harvest	Biu	0-5cm	5.97	151.0	1.50	2.59	6.21	1.40	0.26	0.55
		5-10cm	6.02	94.3	1.03	1.78	7.97	1.40	0.26	0.31
		10-20cm	6.12	85.6	0.92	1.59	7.85	1.80	0.22	0.23
	<b>Total</b>	<b>18.1</b>	<b>339.0</b>	<b>3.45</b>	<b>5.96</b>	<b>22.0</b>	<b>4.60</b>	<b>2.72</b>	<b>1.09</b>	
Post- Harvest	Biu	0-5cm	6.32	76.0	1.58	4.16	90.9	37.0	0.12	2.94
		5-10cm	6.14	39.0	1.31	4.09	58.7	29.6	0.12	1.54
		10-20cm	6.16	28.0	1.21	4.17	83.9	35.4	0.13	1.79
	<b>Total</b>	<b>18.6</b>	<b>143.0</b>	<b>4.10</b>	<b>12.4</b>	<b>234.0</b>	<b>102.0</b>	<b>0.37</b>	<b>6.27</b>	

**DISCUSSION**

Table 2 gives predominant high concentrations of manganese and iron in all the depths for the harvests periods, this could be associated to nature of soil of the area which are mostly found amongst or surrounded by scattered rocks. It is also clearly observed that the concentration of the heavy metals is higher in the post-harvest compared to pre-harvest. This could be attributed to the use of agrochemicals applied to boost harvest and to control pest, since in the

formulation of fertilizers heavy metals are involved as reported by the association of American plant food control officials (AAPFCO, 2007) which established rules and standards in regard to heavy metals in fertilizer. According to the uniform state fertilizer bill, fertilizers that contain guaranteed amounts of phosphates and/or micronutrients are adulterated when they contain metals in amounts greater than the levels of metals established in Table 4.

**Table 4. Maximum heavy-metal levels allowed in fertilizer (AAPFCO, 2007)**

Metals	ppm per 1% P <sub>2</sub> O <sub>5</sub>	Micronutrients
Arsenic	13	112
Cadmium	10	83
Cobalt	136	2228
Lead	61	463
Mercury	1	6
Molybdenum	42	300
Nickel	250	1,900
Selenium	26	180
Zinc	420	2,900

Metals such as lead, arsenic, cadmium, copper, zinc, nickel, and mercury are continuously being added to our soils through various agricultural activities such as agrochemical usage and long-term application of urban sewage sludge in agricultural soils, industrial activities such as waste disposal, Waste incineration and vehicle exhausts, together with anthropogenic sources. All these sources cause accumulation of metals and metalloids in our agricultural soils and pose threat to food safety issues and potential health risks due to soil to plant transfer of metals (Khan, 2005). Investigations of heavy metal migration and accumulation in natural conditions are very laborious as it is difficult to control all numerous factors influencing metal behaviour in the field (Ermakov *et al.*, 2007).

It is also observed in figure 1 the decrease in heavy metals concentration with increase in depth which is in agreement with increase in pH with increase in depth. Low pH increases the solubility and mobility of heavy metals as reported by LaBauve *et al.* (1988) that the mobility and availability of heavy metals is considerably greater in acidic soils than in near neutral or alkaline soils. In this study organic carbon and organic matter were observed to decrease with depth both in the pre-harvest and post-harvest, hence this justifies the retention of the heavy metals at the lower surfaces as reported by La Bauvee *et al.* (1988) and by Lawan *et al.* (2023) that high organic matter content helps in high retention capacity of many pollutants. This study is in agreement with Akan *et al.*, 2013 reported that cation exchange capacity

(CEC) of a soil increases with a rise in pH. In study, the CEC is found to decrease in depth with rise in pH. Levels of Na, Ca and K detected in the soil are within the safe limit set by FAO, however, the heavy metals were found to be above the limit.

**CONCLUSION**

The concentration of the heavy metals is higher in the post-harvest compared to pre-harvest. This could be attributed to the use of agrochemicals and other soil amendments applied to boost harvest and to control pest, since in the formulation of fertilizers heavy metals are involved. The decrease in heavy metals concentration with increase in depth is in agreement with increase in pH with increase in depth. Low pH increases the solubility and mobility of heavy metals since the mobility and availability of heavy metals is considerably greater in acidic soils than in near neutral or alkaline soils. In this study organic carbon and organic matter are observed to decrease with depth both in the pre-harvest and post-harvest, hence this justifies the retention of the heavy metals at the lower surfaces since high organic matter content helps in high retention capacity of many pollutants. In study, the cation exchange capacity (CEC) is found to decrease in depth with rise in pH. Levels of Na, Ca and K detected in the soil are within the safe limit set by FAO, however, the heavy metals were found to be above the limit.

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