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Comparative Studies of Heavy Metals and Mineral Residues in Some Farm Crops around Mining Community of Ribi, Awe Local Government Area of Nasarawa State

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***Abstract*— *This work investigated the level of heavy metals and other elements present in two agricultrural crops (millet and maize) cultivated in mining community of Ribi, Awe LGA of Nasarawa State, Nigeria. Samples were collected from four (4) different farms at the peak of rainy season (between July and August). Samples were analysed at the Chemistry Advance Research Centre, Sheda Science and Technical Complex (SHESTCO) Gwagwalada Abuja. The atomic absorption spectrometer (thermo Scientific, ice3000AA02134104v1.30) was used. All analyses were performed in triplicate. Data were analysed using Minitab Statistical software (16.0). In the rainy season, millet had higher concentration of all the residues quantified except in cadmium which was more concentrated in maize (0.11mg/L). In other heavy metals, lead was 2.83mg/L in millet and 2.54mg/L in maize. Copper was 1.32mg/L in millet and 0.83 in maize. Magnesium was 10.47mg/L in millet and 10.43mg/L in maize. In the dry season, maize had higher concentrations of lead (2.67mg/L), copper (0.925mg/L), nickel (0.134mg/L) and iron (1.688mg/L) whereas cadmium, magnesium, and zinc were more in millet than in maize. Dry season millet was higher in some residues than the control millet. Some millet residues were higher in rainy season than the control level. In millet, lead was highest in raining season (2.831 mg/L) whereas copper and cadmium were very high in dry season (0.586 mg/L and 0.213mg/L respectively), even more than the control. Magnesium residues recorded the highest values among all heavy metals present in millet. Magnesium also had the highest concentration among the residues present in maize in the following order: rainy season (10.43mg/L) > dry season (9.33mg/L) > maize control (9.23mg/L). Iron was more concentrated in the control maize (2.65mg/L) than in both dry and rainy seasons whereas zinc recorded higher seasonal concentrations (0.44mg/L) than the control level (0.46mg/L The values of Pb, Zn, and Ni in millet and maize are above the WHO's standard guideline while other residues are within or below the regulatory limits. Mining activities taking place around the in the study location might have impacted negatively on the safe consumption of agricultural crops cultivated by farmers.*

Keywords*— *Heavy metals, Mineral residues, Millet, Maize, Mining.

I. INTRODUCTION

Heavy metals are metallic elements which have a high atomic weight and a density much greater (at least 5 times) than that of water and is harmful to most organisms even when present at low concentration (Amin *et al.*, 2003). Toxic heavy metals comprise a group of minerals that have no known function in the body and are harmful to humans (Amin *et al.*, 2003). Heavy metals exist in natural and contaminated environments and cannot be easily detoxified via degradation, resulting in their persistence in the environment.

Many of these metals, such as Cd, Pb and Cr, are carcinogens and are involved in several diseases, including Alzheimer's, Parkinson's, multiple sclerosis, osteoporosis, developmental disorders and failure of several organs (e.g., heart, kidney, lungs, immune system) (Duruibe *et al.*, 2007). In mining areas, where exploration activities are carried out, there has been an increased level of toxic metals in water and agricultural soils with a resultant increased uptake and deposition on foods (including processed foods) such as cereals, and vegetables thus posing serious health implications to the consumers (Duruibe *et al*., 2007).Different studies have shown varying amounts of heavy metals in various food sources in Nigeria (Edward *et al*., 2013).

Contamination and subsequent pollution of the environment by toxic heavy metals have become an issue of global concern due to their sources, widespread distribution and multiple effects on the ecosystem as well as their cumulative behavior, toxicity and potential hazardous effects not only on crop plants but also on human health (Oluyemi *et al*., 2008). The situation is even more worrisome in the developing countries where research efforts towards monitoring the environment have not been given the desired attention by the stake holders (Oluyemi *et al*., 2008). Excessive accumulation of heavy metal in agricultural land through vehicular emissions may results in soil contamination and elevated heavy metal uptake by crops, and thus affects food quality and safety and human health (Miclean *et al*., 2007). This work therefore investigated the heavy metals and concentration of toxic elements present in two agricultrural crops cultivated in mining community of Ribi, Awe LGA of Nasarawa State, Nigeria.

II. MATERIALS AND METHODS

The samples were randomly selected within the community where mining and agricultural activities are predominantly practice " collections were done around four notable areas within the community

Experimental samples

The cereal crops (maize and millet) analyzed were collected from four (4) different farm sat the peak of rainy season (between July and August) and dry season around November in Ribi Community in Awe local government area of Nasarawa state. The reason for choosing Ribi community was because its mining nature as well as persistence farming activities. A total of (4) four samples were gathered with each sample randomly hand-picked in a big brown envelope and labelled. The samples were cleaned by sieving and hand separation to remove extraneous materials.

Sample preparation

Analytical reagents (AnalaR) grade chemicals and distilled water were used throughout the study. All glassware plastic containers that were used in this work were washed with detergent solutions followed by 20% (u/v) nitric acid and then rinsed with tap water and finally with distilled water. At the end of the drying, the oven was turned off. The sample was left overnight to enable the sample to cool to room temperature. Each sample was grounded into powder, sieved and stored in a 250cm^3 screw capped plastic jar and appropriately labelled.

Digestion procedure

The 2g of grounded sample was weighed out into100ml standard flask made up to mark with de-ionized water The grounded sample was mixed with 10ml of concentrated nitric acid.

Determination of heavy metal concentration in plants samples

Samples were taken to Chemistry Advance Research Centre, Sheda Science and Technical Complex (SHESTCO) Km 10 Kwali-Abuja Road Gwagwalada for analysis.The mineral elements were analyzed with atomic absorption spectrometer (thermo Scientific, ice3000AA02134104v1.30) equipped with air-acetylene flame. 100ml standard flask was used to filter the digest. The concentration of metals Mg, Pb, Cu, Cd, Fe and Zn samples digests was determined by interpolation while the coding, A= millet control, B= millet dry season, C= maize rainy season, D= maize dry season, E= maize control, F= millet rainy season were used.

Statistical analysis

All analysis was performed in triplicate. Results of heavy metal concentrations in the analysed Crop samples were entered into Microsoft Excel, 2011. Data were transferred into Minitab Statistical software (16.0) for analysis. Data were grouped into segments and described appropriately. Results were presented in Tables, Bar charts, Line plots and Box plots. Inferences were made using: Two ways ANOVA and Two sample T-tests at 95% confidence limit Pearson's correlation was carried out to determine the relationships among heavy metal residues.

III. RESULTS AND DISCUSSIONS

In millet, lead was highest in raining season (2.831 mg/L) whereas copper and cadmium were very high in dry season (0.586 mg/L and 0.213mg/L respectively), even more than the control. Nickel content in both dry and rainy seasons were lower than the control level of 0.162mg/L (Table 1).

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Table 1: Selected Heavy Metal Residues (Lead, Copper, Cadmium and Nickel) in Millet in Dry and Rainy Seasons

Residues	Millet control (mg/L)	Millet dry season (mg/L)	Millet rainy season (mg/L)
Pb	2.678	2.197	2.831
Cu	0.112	0.586	1.132
Cd	0.108	0.213	0.091
Ni	0.162	0.111	0.15

F (Control, Dry and Rainy seasons) = 1.16, P>0.374 (P>0.05)

As presented in Table 2, magnesium residues recorded the highest values among all heavy metals present in millet. Magnesium in millet was 10.361 mg/L in dry season, lower than the 10.47mg/L in rainy season. Both residues were higher than the control residue (10.329 mg/L). Millet iron contents in dry and rainy season (1.577 mg/L and 1.523 mg/L) were lower than the control level of 2.517mg/L. Similarly, zinc contents in both seasons were also lower than the control level of 0.694mg/L. Seasonal variation and control variables yielded similar results in heavy metal residues (F= 1.20, P>0.05). Figure 1 shows the spectrum of heavy metal residues in millet across two seasons and the control. The top three residues were magnesium, lead and iron. Nickel and cadmium levels were very minute. In rainy season, copper level was far higher than in both dry season and control millet. Among the seven heavy metals investigated, only iron, zinc and nickel residues were higher in control millet than either or both seasonal millets. In other four residues, seasonal results were higher than the control millets.

Table 2: Selected Heavy Metal Residues (Magnesium, Iron and Zinc) in Millet (Dry and Rainy Seasons)

Residues	Millet control (mg/L)	Millet dry season (mg/L)	Millet rainy season (mg/L)
Mg	10.329	10.361	10.47
Fe	2.517	1.577	1.523
Zn	0.694	0.513	0.54

F (Heavy metal residues) = 831.34, P=0.000 (P<0.05)
F (Control, Dry and Rainy seasons) = 1.20, P=0.391, P>0.05

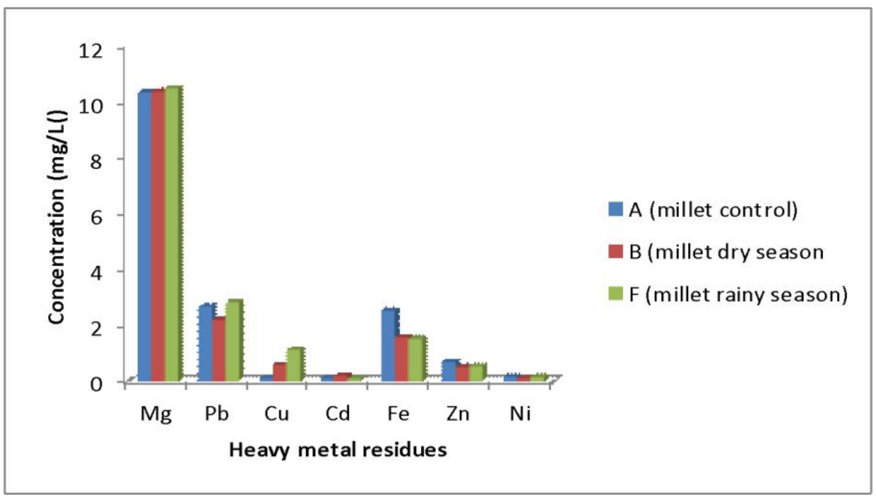

Fig.1: Spectrum of Heavy Metal Residues in Millet across two Seasons

Table 3 gives the concentrations of lead, copper, cadmium and nickel in maize. Lead content was the highest among them recording 2.666mg/L in dry season and 2.538mg/L in rainy season and both values were higher the control maize

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(2.49 mg/L). Copper level was higher in control variable (1.132mg/L) than in seasons. Although cadmium level was relatively low in maize, the amount obtained in rainy season (0.112mg/L) was above the dry season and control. Maize nickel level (slightly raised above cadmium) was almost the same in control, dry and rainy season (0.13mg/L). Seasonal variables and control gave similar results in heavy metal residues in maize (F= 0.42, P=0.677).

Magnesium had the highest concentration among the residues present in maize in the following order: rainy season (10.43mg/L) > dry season (9.33mg/L) > maize control (9.23mg/L) as shown in Table 4. Iron was more concentrated in the control maize (2.65mg/L) than in both dry and rainy seasons whereas zinc recorded higher seasonal concentrations (0.44mg/L) than the control level (0.46mg/L). Statistically, control variable, rainy and dry season produced similar results (F= 0.17, P>0.05). Figure 2 reveals the spectrum of heavy metals in maize. Similar to those in millet, maize had very high concentration of magnesium followed by lead, iron and copper and zinc. Cadmium and nickel levels were much reduced. In copper and iron, values in rainy and dry seasons were below the control level. In other residues, seasonal values were above the control.

Table 3: Selected Heavy Metal Residues (Lead, Copper, Cadmium and Nickel) in Maize (Dry and Rainy Seasons)

Residues	Maize control (mg/L)	Maize dry season (mg/L)	Maize rainy season (mg/L)
Pb	2.49	2.666	2.538
Cu	1.132	0.925	0.831
Cd	0.092	0.091	0.112
Ni	0.134	0.134	0.136

F (Heavy metal residues) = 424.95, P=0.000
F (Control, Dry and Rainy seasons) = 0.42, P=0.677

Table 4: Selected Heavy Metal Residues (Magnesium, Iron and Zinc) in Maize (Dry and Rainy Seasons)

Residues	Maize control (mg/L)	Maize dry season (mg/L)	Maize rainy season (mg/L)
Mg	9.23	9.33	10.43
Fe	2.645	1.688	1.326
Zn	0.441	0.455	0.455

F (Heavy metal residues) = 176.03, P=0.000
F (Control, Dry and Rainy seasons) = 0.17, P=0.851

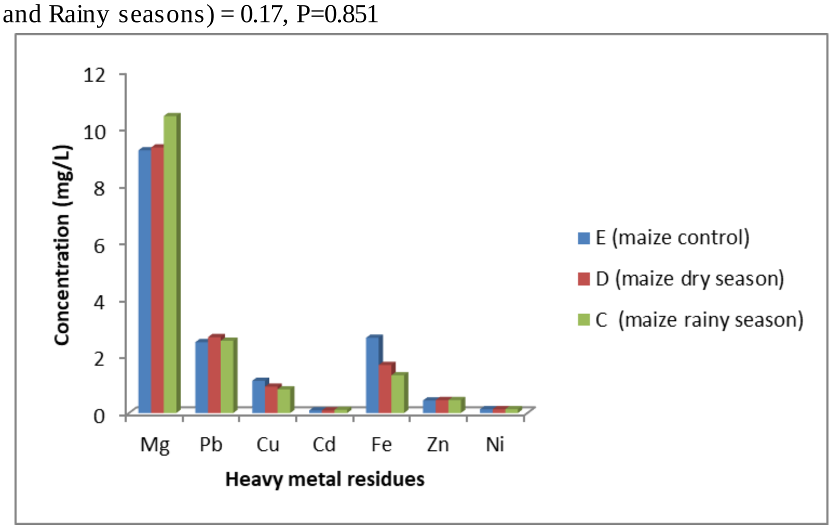

Fig.2: Spectrum of Heavy Metal Residues in Maize across Two Seasons

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Comparing heavy metal residues in maize and millet in rainy season (Table 5) showed that millet had higher concentration of all the residues quantified except in cadmium that was more concentrated in maize (0.11mg/L). In other heavy metals, lead was 2.83mg/L in millet and 2.54mg/L in maize. Copper was 1.32mg/L in millet and 0.83 in maize. Magnesium was 10.47mg/L in millet and 10.43mg/L in maize.

Table 6 compares heavy metal residues in maize and millet in dry season. Maize had higher concentrations of lead (2.67mg/L), copper (0.925mg/L), nickel (0.134mg/L) and iron (1.688mg/L) whereas cadmium, magnesium, and zinc were more in millet than in maize.

Table 5: Comparison of Heavy Metal Residues in Maize and Millet in Rainy Season

Residues	Maize rainy season (mg/L)	Millet rainy season (mg/L)
Pb	2.538	2.831
Cu	0.831	1.132
Cd	0.112	0.091
Ni	0.136	0.15
Mg	10.43	10.47
Fe	1.326	1.523
Zn	0.455	0.54

T= -0.07, P-Value = 0.949, DF = 11

Table 6: Comparison of Heavy Metal Residues in Maize and Millet in Dry Season

Residues	Maize dry season (mg/L)	Millet dry season (mg/L)
Pb	2.666	2.197
Cu	0.925	0.586
Cd	0.091	0.213
Ni	0.134	0.111
Mg	9.33	10.361
Fe	1.688	1.577
Zn	0.455	0.513

T = -0.02, P = 0.984, DF = 11

As given in Table 7, dry season millet was higher in some residues than the control millet. These include: magnesium (10.36mg/L), copper (0.586mg/L) and cadmium (0.213mg/L) in dry season. However. Millet control was higher than dry season millet in lead, iron, zinc and nickel. No statistical significant differences exist in heavy metal concentrations between millet control and the dry season type (t= 0.08, P = 0.941).

Table 8 reveals some millet residues that were higher in rainy season than the control level. Magnesium level was 10.47mg/L and 10.33 in control. Others are: lead (2.83mg/L in rainy season as against 2.68mg/L in control), copper (1.13mg/L in rainy season as against 0.11mg/L in control). Heavy metals below the control level in millet are: cadmium, iron, zinc and nickel . There are no significant differences in the values of heavy metal residues recorded in both millet types (control and rainy season) (t = 0.01, P = 0.992). Statistical uniformity in quantification of heavy metals in the two millet types.

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Table 7: Comparison of Heavy Metal Residues in Millet (Control and Dry Season)

Residues	Millet control (mg/L)	Millet dry season (mg/L)
Mg	10.329	10.361
Pb	2.678	2.197
Cu	0.112	0.586
Cd	0.108	0.213
Fe	2.517	1.577
Zn	0.694	0.513
Ni	0.162	0.111

T-Value = 0.08, P = 0.941, DF = 11

Table 8: Comparison of Heavy Metal Residues in Millet (Control and Rainy Season)

Residues (mg/L)	Millet control (mg/L)	Millet rainy season (mg/L)
Mg	10.329	10.47
Pb	2.678	2.831
Cu	0.112	1.132
Cd	0.108	0.091
Fe	2.517	1.523
Zn	0.694	0.54
Ni	0.162	0.15

T = -0.01, P = 0.992, DF = 11

As shown in Figure 9, the control line (blue line) is below many residues but slightly raised in copper. The control line is widely raised in iron level. Generally, the two lines (control and total maize residues in combined season) are convergent at many points but divergent around magnesium, copper and iron.

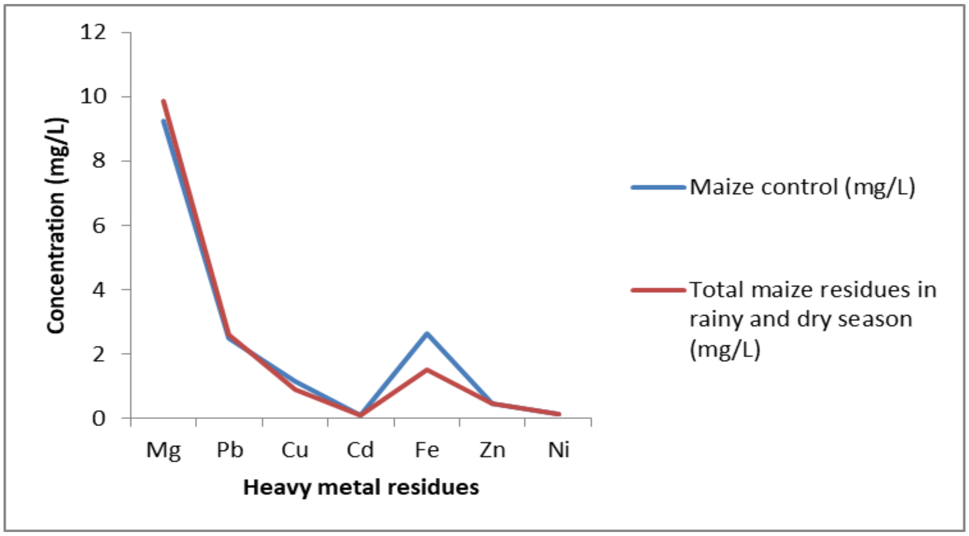

Fig.9: Total heavy metal residues in maize (combined seasons)

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Figure 10 shows much similarity in the millet control line (blue) and the total residues in combined season line (red) most especially in magnesium and lead. Copper residues were far above the control line. However, iron level was far belo w the control line. Zinc and nickel levels are slightly below the control line

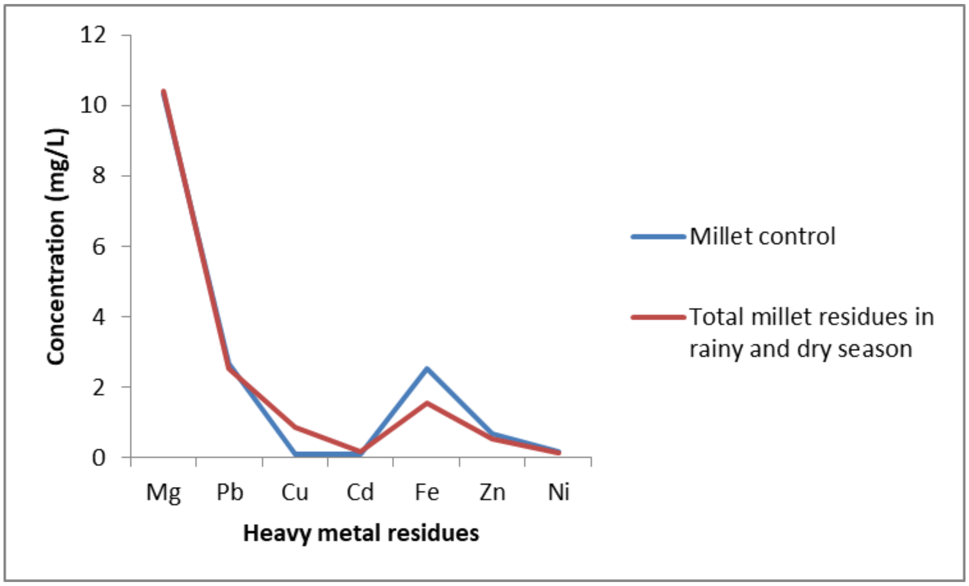

Fig.10: Total heavy metal residues in millet (combined seasons)

According to (Turpeinen (2002), sources of metals contamination can be divided into five major groups: mining, smelting, industry, atmospheric deposition, agriculture and waste disposal The Lead concentration in millet across season was higher than WHO permissible limit (0.01mg/l). This could be as a result of mining activities that introduced Lead to the soil and subsequently to the Millet in the study area. Young children are particularly vulnerable to the effect of Lead and can suffer profound and permanent adverse health effect, particularly affecting the development of the brain and nervours system. Lead also causes long term harm in adults including increased risk of high blood pressure and kidney damage. Similar findings were reported by Ahmed and Mohammed (2005) and Okoye *et al*. (2009).

The concentration of Copper in Millet is highest during dry season when compared with rainy season and the control. Aremu *et al*. (2006) reported similar finding on the assessment of some heavy metal content in some selected agricultural products planted along some roads in Nasarawa State. The result shows that millet has higher Copper content during dry season than in rainy season. The high content of Copper (Cu) in millet during the dry season could be due to deposition of Copper on the surface of these grains during mining or production. Although the deficiency of Copper is rare but it can lead to cardiovascular disease and other problems however most Copper in the body is found in the liver, brain, heart and skeletal muscles and it helps the body to form collagen and absorb iron and play a role in energy production (Okoye *et al*., 2009).

The concentration of Cadmium in the millet is lower when compared to Lead and Copper content across season. This aligned with the work of Wyasu *et al*. (2010). Also, the values of concentrations of Cd in cereals are below the WHO standards (Dahiru *et al*, 2013) (Orisakwe *et al*., 2012). The values are also below NESREA standard for Food, Beverage and Tobacco, (2009).

Higher concentration of Magnesium was found in millet during rainy season similar to the finding of Adamu and Bhagwan (2017). This may offer useful benefits to the body. Deficiency of this element causes growth retardation, nausea, muscle weakness and it may affect cardiac function (Mohammed and Ahmed, 2014). The recommended daily intake of magnesium in male adult is 420mg/day and that of female adult is 320mg/day (Mohammed and Ahmed, 2014).

IV. CONCLUSION

The values of Pb, Zn, and Ni in millet and maize are above the WHO's standard guideline while other residues are within or below the regulatory limits. Mining activities taking place around the in the study location might have impacted negatively on the safe consumption of agricultural crops cultivated by farmers.

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