Comparative Assessment of the Levels of Some Metal Ions in Soil Rhizosphere of Onion and Onion Bulb (*Allium cepa l*) Cultivated in Danbam Local Government Area: North East Nigeria

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Abstract: Levels of some metal ions $(Cd^{2+}, Pb^{2+},$ Cr^{3+} , Mn^{2+} and Mg^{2+}) in the soil rhizosphere and onion bulb were determined by spectroscopic techniques (Atomic Absorption Spectroscopy AAS, and UV-Visible Spectrophotometry). Comparative analysis of the results by the two techniques used shows that Cr, Cd, and Pb were not detected by atomic absorption spectrophotometer in both the soil rhizosphere and onion bulbs but Mn was detected at concentrations ranges of 9-12 ppm and 2 - 13 ppm in the soil and onion bulbs. Concentration of Mg^{2+} was observed to range 6 – 10 ppm and 7 -9 ppm in the soil and onion bulb respectively. Much lower concentrations were detected by the spectrophotometric determinations of Cd, Mn, and Pb in both the soil and onion bulb samples with Pb having the highest concentration (0.002 - 0.005 ppm) in the four study sites. Cr was not detected by any of the two techniques used.

Key Words: Allium cepa L. Determination, metal ions, soil rhizosphere, onion bulb, spectroscopic techniques

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1.0 Introduction

The soil has been remarked as a major sink for heavy metals and from the soil, plant can accumulate heavy metal ions through the process of foliar absorption (Eddy et al., 2004)). Soil rhizosphere is the layer or region of the soil that is directly influenced by root secretions and associated soil microorganisms. The presence of high concentration of some heavy metals in the soil rhizosphere will likely impart toxic effect on plants. Such high concentrations may be natural to the soil or consequences of anthropogenic, agricultural and industrial activities (Bystricka et al., 2015; Shabanda and Kabiru, 2015; Smith, 2009). Li et al. (1994) reported significant concentration of Mg²⁺ and Co²⁺ ions on the cell division and the nucleolar cycle mitosis in the root tip cells of Allium cepa and Liu and co-workers (1994) observed that high concentrations of both ions imparted toxic effect cell division etc. Lead is one of the commonest toxic heavy metal in the environment (Lewis, 2010). Several entrace routes have been reported for lead ion including absorption from the soil and atmospheric deposition on leaves (and eventual assimilation) (Tan and Nguyem, 2010) Consumption of lead contaminated fruits and vegetables can be consumed by man or animals and become loaded with higher lead concentration. (Lewis, 2010; Nas and Ali, 2018). Cadmium is another toxic heavy metal that are also common in most environments because it can be readily absorbed by plants and is known to impart on the synthesis of chlorophyl (Oves et al, 2016). Apart

from their impact on consumers, heavy metal ions can also affect primary producers. For example, Ishikawa et al (2006) found heavy metal contamination as a common factor restricting plant growth in different agro-climatic regions. They observed that Cr(VI) in plant tissues has strong tendency to induced some changes that slowed down plant growth etc. The presence of cadmium and lead has been reported as a barrier to the smooth operation of oxygen path way in both plants and animals (Shabanda and Kabiru 2015; Zhang et al., 2017). On the other hand, manganese (Mn) and some chromium ions (except Cr(VI)) are essential enzymes activators in both plant and animals (Wuana and Okieimen, 2011). For example, manganese can convert nitrogenous waste products into urea and chromium maintains the correct level of glucose in the blood.

Evidences abound on the distribution of heavy metals in different parts of plants or animals indicating that different plant tissues have different receptive characteristics for different heavy metals. Therefore, the aim of the study was to assess the concentration levels of Pb, Cr, Cd, Mn and Mg in the soil rhizosphere and in onion bulbs.

2.0 Materials and methods

2.1 Sampling sites

The study areas were Kwadatala, Tingariye, Kaderi and Ganjiwa of Dambam Local Government Area of Bauchi State, Nigeria. Dambam Local Government Area is located within Misau Emirate of Bauchi State covering an area of about 1,077 square kilometers within longitude 10. 71^o and latitude 11.68^o.

Four (4) different soil rhizospheres together with their onion bulb samples were collected from four locations in the Local Government where onions are grown and were labeled as in Table 1.

Table 1: Sample classification/labeling							
Sample Location	Soil Samples	Onion samples					
Kwadatala	S1	A1	-				
Tingariye	S2	A2					
Kaderi	S 3	A3					
Ganjiwa	S4	A4					



2.2 Determination of metal ions by AAS

Each soil sample (10 g) was first weighed and crushed using a wooden mortar and pestle and sieved so as to obtain fine soil particles, out of which 8 g was re-weighed and kept in a sample container. The onion bulbs were grinded using an electric blender, dried to constant weight and blended to powdered form.

One (1 g) gram of each of the eight dried samples (i.e. four soil rhizosphere samples and 4 onion samples) were respectively placed in different 250 cm^3 beakers and then heated in a fume cupboard according to the method reported by Shabanda and Kabiru (2015).

2.3 Preparation of stock solution and standard solutions

A 1000 ppm stock solution was prepared by dissolving 1 g each of the metal (Cd 99.9%, Pb, Mg, Mn and Cr) into separate 1-L volumetric flasks and diluted to the mark with deionized water.

2.4 Determination of metal ions in the soil rhizosphere samples

Ten (10) 10 cm³ of concentrated HNO₃ (65%) was added to the soil sample in the 250 cm³ beaker, covered with a watch glass and heated for 45 minutes until a dark brown colour was observed. The watch glass was removed and heated for 15 minutes to dryness during which brown fumes were given off. 10 cm³ aqua regia (in molar ratio of 1:3 HNO₃:HCl:) were added to the residue and heated to dryness again for 10 minutes and yellowish-brown residue obtained was re-dissolved in 10 cm³ of 1M HNO₃ and re-heated to drvness to obtain a whitish-vellow residue After cooling, 10 cm³ of deionized water was added and stirred. The mixture was filtered into 50 cm³ volumetric flask and then the solution was diluted to the mark with de-ionised water. A vellowish-brown solution was obtained. The metal ions Cd, Pb, Mg, Mn and Cr were analyzed by AAS machine and their concentrations were determined from a calibration curve

2.4.1 Determination of metal ions in the onion bulb samples

1 g of the onion bulb sample was taken in a 250 cm³ beaker to which 10 cm³ conc. HNO₃ (65%) were added and then covered with a watch glass. It was then heated for 45 minutes. A dark brown solution was obtained. The watch glass was removed and then the solution was heated until a cream-milky residue was obtained. 10 cm³ of aqua regia were added and

the solution was heated to dryness after which a yellowish-brown residue was obtained. The residue was re-dissolved in 10 cm^3 of $1M \text{ HNO}_3$ and again heated to dryness after which a whitish-yellow residue was obtained. 50 cm³ of deionized water were added, stirred and filtered into a 50 cm³ volumetric flask. A brown solution was obtained and then diluted to mark with deionized water. The metal ions were then analyzed by AAS as before.

2.5 Spectrophotometric determinations of the metal ions.

Pb was determined using the method reported by Jeffery, et al. (1989).

2.5.1 Preparation of ammonia-cyanidesulphate solution

In order to prepare ammonia cyanide sulphate solution, sodium sulphate (0.15g) was weighed and transferred into a 100 cm³ volumetric flask containing 35 cm³ of concentrated ammonia solution (98.5%) and 3 cm³ of 10% potassium cyanide solution was also added and the mixture was diluted to mark with deionized water.

2.5.2 Determination of Molar Absorptivity of Pb Lead nitrate (0.008g) was dissolved in 1 dm³ of deionized water. 10 cm³ of the solution was into 250 cm³ separating funnel, then 75 cm³ of ammonia cyanide sulphate solution were added and the pH was adjusted to 9.5 by addition of 9.4 cm³ od concentrated HCl and 7.5 cm³ of 0.005% solution of dithizone in chloroform was added. This was succeeded by addition of 17.5 cm³ of chloroform (99.5%). The mixture was shaken for 1 minute and allowed to settle for 30 minutes. The mixture was observed to be separated into orange and dark green coloured upper and lower layers. The absorbance of the upper layer was measured at 510 nm against the ammonia -cyanide sulphate solution as a blank solution in a 1.0 cm absorption cell using a uv-visible spectrophotometer model 752 N. Further extraction of the same solution was made by adding 75 cm³ of ammonia cyanide sulphate solution which gave approximately zero absorbance as an indication that the extraction was complete.

2.5.3 Determination of Pb in the samples

10 cm³ of the digested sample was measured into 250 ml separatory funnel. 75 cm³ ammonia cyanide sulphate solution was added and the pH was adjusted to 9.5 using HCl. This was followed by addition of 7.5 cm³ of 0.005% solution of dithizone in chloroform and 17 cm³ of chloroform was also

added. The mixture was shaken for one (1) minute and allowed to settle. After 30 minutes, the mixture separated into orange and dark green upper and lower layers respectively. The absorbance of the upper layer was measured at 510 nm using 1.0 cm cell against ammonia cyanide sulphate solution as the blank The absorbances for each sample were measured and the concentrations were calculated through extrapolation to the calibration curve that was plotted according to Beer-Lambert:s law. the application of Beer-Lambert's law of spectrophotometry.

3.4 Determination of Cd^{2+} in the samples

Stock solution of cadmium was prepared using cadmium metal dissolved in trioxo nitrate (V) acid. Spectrophotometric determination of cadmium ion was achieved by first adding 20 µl of perchloric acid was added and 20 μ l of thymol blue solution (0.1%) into 10 ml of the digested sample. The pH was adjusted to 1.24 using 20% NaOH solution. 5 cm³ of 1% potassium cyanide and 1 cm³ of hydroxylamine hydrochloride solution were also added. 15 cm^3 of the solution extract I (0.08g) of dithizone in 1-L chloroform) was added then the mixture was shaken for 1 minute. After separation, the lower layer (dark green) was tapped to another separatory funnel containing 25 cm³ of tartaric acid (2%) and shaken for 1 minute, while settling, 15 cm³ of solution extract I was added again to the solution that was left in the first separatory funnel and shaken for 1 minute. Both the lower layers in two separatory funnels (with excess of dithizone) were discarded and the solutions were mixed in one separatory funnel and 5 cm³ of chloroform was added and for 1 minute before allowing it to settle. The chloroform was discarded and 1 cm^3 of hydroxylamine hydrochloride was added together with 15 cm³ of extract II (0.008g of dithizone in 1-L chloroform) and 5 cm³ of 0.05% KCN. After sedimentation, the dithizone was removed and the absorbance was measured using 357 nm as the reference wave length. 3.5 Simultaneous **Spectrophotometric**

Determination of Mn and Cr

Cr and Mn were simultaneously determined by a method reported by Jeffery and Basset (1989)

3.0 Results and Discussions

Results obtained from atomic absorption spectrophotometer and from UV-visible spectrophotometer for the concentrations of heavy



metals in soil rhizophore, onion bulbs and literature values are recorded in Tables 2 and 3 respectively.

A comparative analysis of the concentrations of the metal ions in the soil and in the onion bulb indicated that Cr, Cd and Pb were not detected by both AAS and spectrophotometry but Mn and Mg were detected by the two techniques in both the soil

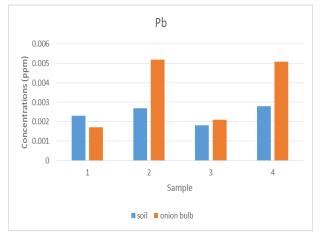
rhizosphere and the onion bulb. The concentrations for Mg in the soil samples were higher than those in the onion bulbs. These were within the range 9.00 - 14.5 ppm and 2.00 - 4.00 ppm. A comparison between the concentrations of the metal ions are represented in Figs. 1, 2 and 3

Site	Cr (ppm)		Mn (ppm)		Mg (ppm))	Cd (ppm)		Pb (ppm)	
-	Soil rhizospher	Onion bulb								
	e	ouio	e	ouio	e	buib	e	buib	e	ouio
S1	ND	ND	9.2	2.3	5.7	7.2	ND	ND	ND	ND
S2	ND	ND	12.2	3.12	6.3	8.9	ND	ND	ND	ND
S3	ND	ND	14.5	3.58	10.2	6.98	ND	ND	ND	ND
S4	ND	ND	9.3	1.97	8.5	5.73	ND	ND	ND	ND
Mean	ND	ND	11.3	2.7	7.7	7.2	ND	ND	ND	ND
Var			6.4867	0.5455						
X**	-	3.33	-	13.40	-	-	-	0.005	-	0.78
(TT state	T • 4	1		1 77 1			• \			

(X** = Literature value (Shabanda and Kabiru, 2015, var = variance) Table 3: Concentrations of metal ions obtained from by spectrophotometry

Site	Cr (ppm)		Mn (ppm)		Cd (ppm)		Pb (ppm)	
	Soil	Onion	Soil	Onion	Soil	Onion	Soil	Onion
	rhizosphere	bulb	rhizosphere	bulb	rhizosphere	bulb	rhizosphere	bulb
S1	ND	ND	19.11	12.2	1.27	4.06	2.3	1.7
S2	ND	ND	6.15	12.2	70.5	149	2.7	5.2
S3	ND	ND	21.09	27.5	4.05	102	1.8	2.1
S4	ND	ND	52	10.0	22.2	79.6	2.8	5.1
Mean	ND	ND	24.59	15.48	24.51	83.67	2.40	3.53
Variance			377.8725	65.3425				
X**	-	3.33	-	1.55	-	0.003	-	-

(X** = Literature value (Shabanda, 2015))



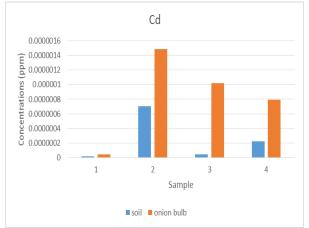


Fig 1: Concentrations of Pb in Soil Rhizosphere and the Onion Bulb

Fig 2: Concentrations of Cd in Soil Rhizosphere and the Onion Bulb



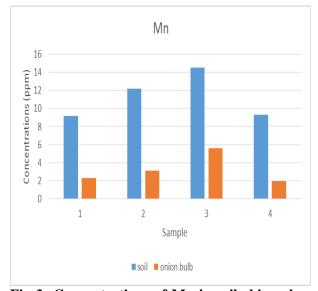


Fig 3: Concentrations of Mn in soil rhizosphere and the onion bulb

However, results obtained for Mg ions were within the range 6.00 - 10 ppm in both the soil rhizosphere and the onion bulb. The observed depletion of the concentration of Mg in the soil rhizosphere may be attributed to the utilization of the metal for the formation of the green pigments (chlorophyll) by the plant. Also, if the soil is saturated with magnesium, the observed concentration in the plant is justifiable. However, results obtained from spectrophotometry measurements analysis indicated that the concentrations of the metal ions are lower than those obtained from atomic absorption spectrophotometer. The observed differences could be attributed to analytical factors such as interferences, analytical errors, instrument precision and sensitivity as well as analytical error.

From atomic absorption measurement, it is evident that there is no significant difference between the concentrations of Cr (VI), Cd (II) and Pb (II) in the soil rhizosphere and onion bulb. Mean concentration of Mn^{2+} and Mg^{2+} in the soil were higher than the corresponding concentration in the onion bulb suggesting that the soil acted as a sink for these heavy metals (ref). This also implies that Mn^{2+} and Mg'^{2+} in the onion bulb are absorbed from the soil. Statistical analysis reveals that the sorption of manganese by onion bulb is linear ($R^2 = 0.947$) indicating that the sorption increases as the concentration of Mn^{2+} in the sorption model couldn't be established for the adsorption of Mg^{2+} by the onion.

On the other hand, results obtained from UV-visible spectrophotometry analysis also established the existent of no significant difference in levels of concentration of Cr (VI) in soil rhizosphere and onion bulb but such relationship couldn't be established for Cd²⁺ and Pb²⁺ compared to results obtained from atomic absorption spectrophotometer measurements. However, mean concentrations of Cd^{2+} and Pb^{2+} in the onion bulbs were higher than the corresponding concentrations in the soil. The observed trend seems to be a reversal of the expected trend as observed in the previous results. According to Eddy and Ekop (2007), some plants have the capacity to concentrates heavy metals in their tissue to a level that is far higher than the corresponding concentration in the soil. This trend depends on a number of factors including plant species, pH of the soil, organic matter content of the soil, transpiration rate of the plant and even the physiological functioning of the plant species like the secretion of transporters that aid transport of metals across membranes. Ekwememgbo et al. (2013) also stated that plants that have significant capacity to absorb heavy metal ions from the soil are suitable for employment in phytoremediation study. Therefore, it is necessary for the heavy metal concentrations in the soil to be relatively low in order to reduce the transfer rate since this plant has a strong tendency to draw heavy metal from the soil.

The concentrations of all the metals were found to be below the World Health Organizations standards when compared with the literature values by Shabanda and Kabiru (2015) unlike a similar study by Bedassa, *et al* (2017) in which some selected heavy metals in the onion bulb and onion leaf (*Allium cepa L.*) in selected areas of the Central rift valley of Oromia region of Ethiopia, found Cr to be above the permissible level and concluded that the consumption of onion in that area could pose a health risk.

Although the mean concentration of Mn^{2+} in the soil was higher than the corresponding mean concentration in the onion bulb, there was not significant difference between the two set of data (t_{Calculated} = 0.2411 while t_{Critical} = 2.3534). Correlation between the two set of data was positive (r = 0.24145). Results of statistical analysis obtained for other metals are shown in Table. 4.

There was no significant difference between the results obtained from spectrophotometric and atomic

to concentration of Mn^{2+} , however, negative heavy metal in the soil.

absorption spectrophotometer methods with respect correlation was observed for the concentration of

Table 4: Descriptive statistics for the distribution of heavy metal ions between the soil and onion
bulb

Meatal	t _{Calculated}	t _{Critical}	r	Remark
Mn (AAS)	0.7999	2.3534	0.2414	No significant difference in mean concentration and correlation is positive
Cd (AAS)	2.8812	2.3534	0.7728	Significant difference in mean concentration and correlation is positive and significant
Pb (AAS)	-1.4807	2.3534	0.8446	No significant difference in mean concentration and correlation is positive and significant
Mn (Spect)	9.323838	2.3534	0.9736	Significant difference in mean concentration and correlation is positive and significant
Mg (Spect)	0.3200	2.3534	-0.5073	No significant difference in mean concentration and correlation is negative

** results from AAS= atomic absorption spectrophotometer , Spect. = results from spectrophotometric analysis.

4.0 Conclusion

The results and findings of the study reveal that Cd^{2+} . Pb²⁺ and Mn²⁺ have strong tendency to be concentrated in onion bulb. Concentration of some of the heavy metals analysed were higher in the bulb than in the soil. Although statistical significant difference was not observed between the results obtained from AAS and spectrophotometric analytical methods, measured mean concentrations showed some numerical differences indicating that there may be some discrepancies between the two analytical methods.

The outcome of the research shows that concentrations of Cd and Pb ions were only detected by spectrophotometry analysis

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Conflict of Interest

The authors declared no conflict of interest.

