

WERE DETERMINED IN FIVE DIFFERENT PLACES IN KANO STATE, USING VEGETABLE AMARANTH (AMARANTHUS CRUENNSUS L) AND SUNFLOWER (HELIANTHUS ANNUS). THE ANALYSIS WAS DONE, USING ATOMIC ABSORPTION SPECTROPHOTOMER- MODEL 210 VGP **BUCK SCIENTIFIC (AAS).**

RESULTS

IT WAS FOUND THAT IN ALL THE FIVE (5) LOCATIONS OF THE STUDY, THERE EXIST ALL THE EIGHT HEAVY METALS IN VARYING CONCENTRATION, WHICH ARE PRESENTED IN THE FOLLOWING ORDER: (I) FOR THE MONTH OF FEBRUARY THE CONCENTRATION OF THE HEAVY METALS IN VEGETABLE AMARANTH WAS FOUND TO FOLLOW THE ORDER: NI > ZN > MN > FE > CU > PB > CR > CD, WHILE THE CONCENTRATION IN SUNFLOWER WAS FOUND TO FOLLOW THE ORDER ZN > NI > FE > CU > MN > PB > CD >CR.(II) FOR MARCH, THE CONCENTRATION OF HEAVY METALS IN VEGETABLE AMARANTH WAS FOUND TO FOLLOW THE ORDER ZN > FE > CU > NI > MN > PB > CD>CR WHILE THE CONCENTRATION IN SUNFLOWER WAS FOUND TO

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FOLLOW THE ORDER ZN > NI > CU > MN > FE >> CR AND PB > CR > C.

CONCLUSION

IT IS CONCLUDED THAT FOR NAIBAWA, CD, CR, CU, FE, NI, MN, AND PB HAVE HIGH PROBABILITY OF ORIGINATING FROM THE SAME SOURCE WHILE ZN MIGHT HAVE ORIGINATED FROM A DIFFERENT SOURCE (THIS WAS EXPECTED CONSIDERING THE NATURE OF THE NAIBAWA SITE - DUMP SITE). FOR KOFAR RUWA, FE AND ZN RECORDED HIGH PROBABLY OF ORIGINATING FROM THE SAME SOURCE WHILE CD, CR, CU, NI, MN AND PB ARE FROM OTHER SOURCE(S). FOR BUK, CD, CR, CU, FE AND PB ENVIRONMENT ARE PROBABLY FROM THE SAME SOURCE WHILE NI, MN AND ZN MIGHT HAVE BEEN FROM DIFFERENT SOURCE. BUT IN THE CONTROL AREA, THE BUK C SITE, CD, NI, MN, PB RECORDED HAVE PROBABILITIES, INDICATING THEY ARE FROM THE SAME SOURCE WHILE CR, CU, FE AND ZN CONTRARY FROM THE LATTER. IN THE OVERALL SITES, FROM THE DATA GENERATED IT WAS REVEALED THAT CR AND CU ARE FROM THE SAME SOURCE WHILE CD. CR. CU. NI. MN AND PB ARE FROM ANOTHER SOURCE. FROM THE SOIL POLLUTION LOAD INDEX COMPUTED BEFORE, DURING AND AFTER PLANTING THE STUDY INDICATED DECREASE IN THE LEVEL OF CONTAMINATION IN ALL THE SITES.

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Key words: Heavy Metals, Vegetable Amaranth, Sunflower, AAS, and Phythoremediator.

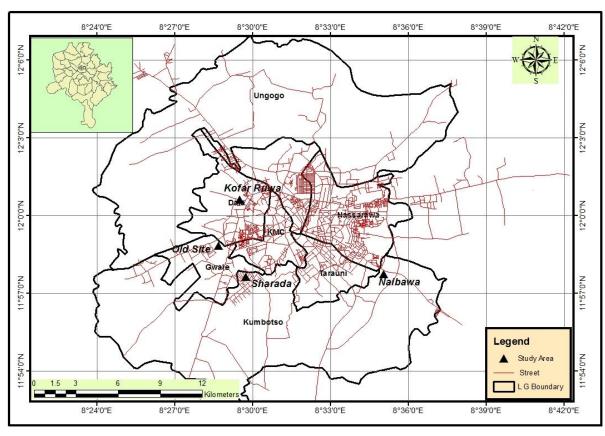
1. INTRODUCTION

Several efforts have been made towards safe-guarding the health of the society by conducting researches on the composition of samples using various techniques. Some of these researches range from identification, determination, study and evaluation of samples (Biological and geological). Natasa et al., (2015) reported that; Melting operation, sludge dumping, intensive agriculture, traffic activities, power transmission, cement - pollution and smelting are possible ways of heavy metal accumulation. Other sources are the bedrock and anthropogenic source (Yeasmin et al., 2013). Metal 22 Contamination in agricultural soil is of increasing concern due to food safety issues and potential health risk (Yeasmin et al. 2013). Heavy Metal pollution has pervaded many parts of the developing countries and affects humans because of 23 their longevity and accumulation in their organs via different ways (Li et al., 2014 and Zhang et al, 2010) The non 24 25 biodegradable of heavy metals and their potential to cause inappropriate effect made them the most noxious material 26 (Seydou and Timoty, 2016). It is widely reported that they have both positive and negative role in human life. The 27 elements play important role in biological process but at high concentrations they may be toxic to biota, disturb the 28 biochemical process and cause hazards. Excessive content of Heavy metals beyond maximum permissible level (MPL) leads to number of nervous, cardiovascular, renal, neurological impairment as well as bone diseases, which significantly 29 30 contribute to decrease human life expectancy (9-10 years) within the affected area and several other health disorders 31 (Yeasmin et al, 2013). Khan et al., reported that National Research Council (NRC) has outlined four steps (processes) in 32 estimating health risk agent, which are hazard identification, exposure assessment, dose/response assessment, and risk 33 characterization. This problem is not an exception in Nigeria as Ahmed et al., (2016) reported the risk level Nigerians and 34 other African countries are exposed to. The scope of this research was restricted to Kano State, Nigeria (within five locations). Kano is a state in Nigeria, located between the latitude 12°15'S and 12°35'N of equator and the longitude 35 8°20'W and 8°27'E of meridian 36

37 In this research the levels of concentrations in the soil in some selected areas within Kano State, Nigeria was 38 investigated. The specific objective in this study is to identify the transfer factors of vegetable amaranth and sunflower, to 39 measure the level of contamination in the soil, and to estimate the level of remediation achieved by the bio-indicators 40 (vegetable amaranth and sunflower). Also to find out whether the metals comes from the same source or not.

41 Figure 1 presents a map of the study areas.

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43 Figure 1: The five (5) selected sample site: Sharada, Kofa Ruwa, Naibawa and Bayero University (two locations) 44 Kano. 45

1.1 THEORETICAL BACKGROUND 46

One of the governing equations that give a relationship between, α (the analyte's absorptivity with units of cm⁻¹ conc⁻¹); 47 Concentration, C; Absorbance, A; and width, b; is the Beer's law (some time called Beer - Lambert Law), presented as 48 49 equation (1):

$$A = \alpha b C \tag{1}$$

If we express the concentration using molarity, then we replace α with the molar absorptivity, ϵ , which has unit of cm⁻¹ M⁻¹ 51 52 . Then, we have: 53

 $A = \varepsilon bC$ (2)

The concentration of heavy metals is directly related to the absorbance of the metals by a substance. al., In this research 54 work we are interested in the Biological and Soil Samples Concentration (C sample), the Plant Concentration Factor (PCF) 55 and Pollution Load Index (PLI). In order to have the concentrations of these metals, the equations used by Udo et al. 56 57 (2009) and Khan et al., (2014) are employed. 58

$$C_1 V_1 = C_2 V_2 \tag{3}$$

60 Where C_n is the concentration of solution and V_n is the volume.

61 Concentration of sample (C sample)

$$C_{sample} = \left(\frac{Abs.}{Standard/Slope}\right) \times \frac{Volume}{Weight of Sample}$$
(4)

64 where Abs. is Reading of absorbance (with respect to Heavy Metals) 65

66 Pollution Load Index (PLI)

$$PLI = \frac{C_{Soil Sample}}{C_{Plant Sample}}$$
(5)

68 Pollution Load Index Soil (PLIs)

69 Ahmed et al., (2013), reported methods used in indicating the level of contamination of soil ranging from low, moderate and severe contamination. The equations are given as: 70

$$C_f = \frac{C_n}{C_r} \tag{6}$$

where C_f is the contamination factor, C_n is the soil concentration and C_r is the background level of the study area. The PLIs is a dimensionless quantity, which depends on C_f . The expression for PLIs is given as:

$$PLIs = \sqrt[n]{C_{f1} + C_{f2} + C_{f3} + \dots + C_{fn}}$$
(7)

75 2.0 Materials and Method

Five (5) experimental sites were set up within Kano State, Nigeria. These are: (a) Bayero University, Kano Screen House (BUK-C) $- 8^{\circ}28'0"$ E & $11^{\circ}59'0"$ N, (b) Bayero University, Kano Environment (BUK-E) $- 8^{\circ}28'0"$ E & $11^{\circ}59'0"$ N (c) Kofar Ruwa (K) $- 8^{\circ}29'5"$ E & $12^{\circ}1'5"$ N,(d) Naibawa (N) $- 8^{\circ}35'0"$ E & $11^{\circ}58'0"$ N and (e) Sharada (S)- $8^{\circ}29'5"$ E & $11^{\circ}58'0"$ N. as shown in Figure 1.

81 **2.1 Samples Preparation, Preservation and Digestion and analysis**

The samples were collected at three growth stages of the five experimental plots at 4th, 5th and 6th months before and after sowing. The samples were then shade-dried for seven days on plastic trays. The dried samples were homogenized by grinding using ceramic coated grinder. The final samples were kept in labeled polythene bags at ambient temperature.

One gram (1g) of the soil samples were weighed into a beaker, and 30ml of Aqua regia (HNO₃ + HCL) was added into the 50ml plastic bottle. The mixture was placed into a mixer (Vibrator) for one hour Thirty Minutes and the mixture was removed. The solution of the mixture (filtrate) was obtained through filtering with Whitman No.42 filter paper. The solution (Suspension) was filled to marke level (50ml) with distilled water. The concentration of Pb, Cd, Ni, Cu, Cr, Zn, Mn and Fe were determined by Atomic Absorption Spectrometry (AAS) - MODEL 210 VGP BUCK SCIENTIFIC. Analysis of each sample was carried out in triplicate and the average was computed.

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93 **3.0 Results and Discussion**

94 **3.1 Samples Concentrations**

95 The concentration of heavy metals is directly related to the absorbance of metals by the samples. From equations 3 which

96 was used to calculate the concentrations of metals in the sample, reveal the need to obtain the Slope/standard.

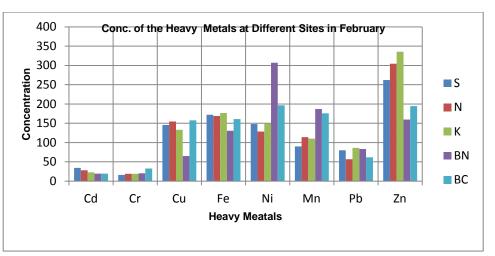
97 3.2 Standard/Slope

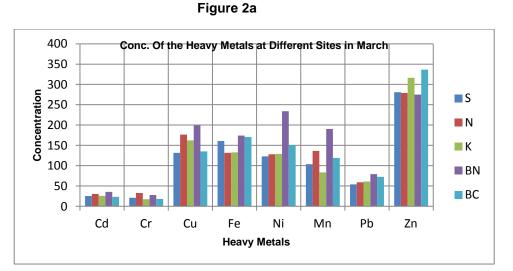
98 The standard/slope for the eight Heavy Metals was computed using equation 4. Different volume of solutions at different 99 concentrations was prepared and analyzed using AAS machine to obtain the absorbance. The concentration and 100 absorbance for each metal are given in **Table 1**.

101	Table 1: Cd, Cr, Cu Fe, Ni, Mn, Pb, and Zn Concentration and Absorbance Values
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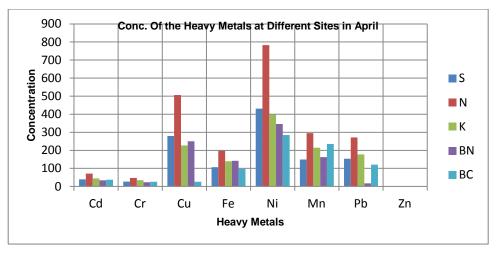
Cadmium (Cd)						
Concentration	01.00	00.80	00.60	00.40	00.20	00.00
Absorbance	00.111	00.087	00.063	00.044	00.023	00.00
		Ch	romium(Cr)	•		
Concentration	01.00	00.80	00.60	00.40	00.20	00.00
Absorbance	00.118	00.097	00.071	00.049	00.026	00.00
		Со	pper(Cu)			
Concentration	05.00	04.00	03.00	02.00	01.00	00.00
Absorbance	00.111	00.088	00.066	00.043	00.022	00.00
		Iro	n(Fe)			
Concentration	10.00	08.00	06.00	04.00	02.00	00.00
Absorbance	00.262	00.212	00.164	00.112	00.054	00.00
		Nic	kle (Ni)			
Concentration	10.00	08.00	06.00	04.00	02.00	00.00
Absorbance	00.131	00.112	00.084	00.053	00.027	00.00
		Mar	nganese(Mn)			
Concentration	10.00	08.00	06.00	04.00	02.00	00.00
Absorbance	00.202	00.162	00.122	00.081	00.042	00.00
		Lea	ad(Pb)			
Concentration	10.00	08.00	06.00	04.00	02.00	00.00
Absorbance	00.223	00.174	00.129	00.086	00.045	00.00
		Zir	nc(Zc)			
Concentration	10.00	08.00	06.00	04.00	02.00	00.00
Absorbance	00.171	00.137	00.102	00.067	00.031	00.00

From **Table 1**, the slopes were deduced with the values as; Cd (0.109), Cr (0.119), Cu (0.022), Fe (0.026), Ni (0.013), Mn (0.02), Pb (0.022) and Zn (0.017) for the eight Heavy metals. Using equation 4 the concentrations were generated and presented in **Figures 2**.







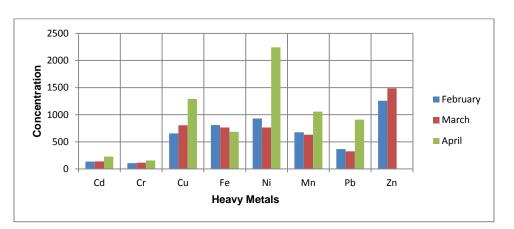






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Figure 3.0: Total concentration of the Heavy Metals for Three Months

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3.2 Correlation of the Eight Heavy Metals. 117

118 These computed concentrations in **Tables 4** and **5** were use to illustrate the correlation between the Heavy Metals using 119 SPS20.0.The tabulated values to illustrate the correlation were given in Tables 2,3,4,5 and 6

120 Table 2: Correlation Matrix of the Heavy Metals from Naibawa sites.

	Cd	Cr	Cu	Fe	Ni	Mn	Pb	Zn
Cd	1.000							
Cr	0.952	1.000						
Cu	0.990	0.900	1.000					
Fe	0.947	0.804	0.983	1.000				
Ni	0.980	0.873	0.998	0.992	1.000			
Mn	0.996	0.923	0.998	0.971	0.993	1.000		
Pb	0.982	0.78	0.999	0.990	1.000	0.995	1.000	
Zn	-0.993	-0.908	-1.000	-0.979	-0.997	-0.999	-0.998	1.000

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122 Table 3: Correlation Matrix of the Heavy Metals from Kofar Ruwa sites.

	Cd	Cr	Cu	Fe	Ni	Mn	Pb	Zn
Cd	1.000							
Cr	0.977	1.000						
Cu	0.985	0.925	1.000					
Fe	-0.376	-0.170	-0.531	1.000				
Ni	0.979	1.000	0.929	-0.178	1.000			
Mn	0.947	0.994	0.876	0.057	0.993	1.000		
Pb	0.943	0.992	0.871	0.047	0.991	1.000	1.000	
Zn	-0.996	-0.996	-0.967	0.296	-0.993	-0.971	-0.968	1.000

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124 Table 4: Correlation Matrix of the Heavy Metals for BUK Environs sites.

	Cd	Cr	Cu	Fe	Ni	Mn	Pb	Zn
Cd	1.000							
Cr	0.873	1.000						
Cu	0.943	0.662	1.000					
Fe	0.753	-0.978	0.492	1.000				
Ni	-0.237	-0.680	0.99	-0.818	1.000			
Mn	-0.339	0.162	0.632	0.364	-0.834	1.000		
Pb	0.412	-0.085	0.691	-0.290	0.788	-0.997	1.000	
Zn	-0.026	0.465	-0.356	0.638	-0.965	-0.949	-0.922	1.000

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128 Table 5: Correlation Matrix of the Heavy Metals for BUK Screen House sites.

	Cd	Cr	Cu	Fe	Ni	Mn	Pb	Zn
Cd	1.000							
Cr	0.353	1.000						
Cu	-0.875	0.144	1.000					
Fe	-0.975	-0.137	0.961	1.000				
Ni	1.000	0.351	-0.876	-0.976	1.000			
Mn	0.986	0.501	-0.784	-0.926	0.986	1.000		
Pb	0.866	-0.162	-1.000	0.955	0.867	0.773	1.000	
Zn	-0.996	-0.433	0.830	0.952	-0.996	-0.997	-0.820	1.000

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132 Table 6: Correlation Matrix of the Heavy Metals for all the sites.

	Cd	Cr	Cu	Fe	Ni	Mn	Pb	Zn
Cd	1.000							
Cr	0.993	1.000						
Cu	0.989	0.993	1.000					
Fe	-0.963	0.989	0.992	1.000				
Ni	0.984	-0.963	0.946	-0.989	1.000			
Mn	0.985	0.985	0.949	-0.902	1.000	1.000		
Pb	0.943	0.990	0.958	-0.915	0.999	1.000	1.000	
Zn	-0.975	-0.975	-0.931	0.879	-0.999	-0.999	-0.997	1.000

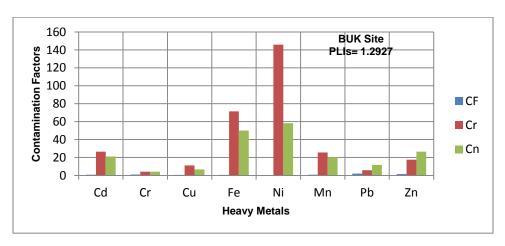
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At Naibawa site, the correlation values obtained indicate that Cd, Cr, Cu, Fe, Ni, Mn, and Pb have high probability of 134 originating from the same source while Zn might have originated from a different source. This is expected, considering the 135 nature of the Naibawa site, the dump site. From Table 3, Kofar Ruwa site shows that Fe is independent from the other 136 137 source while Cd, Cr, Cu, Ni, Mn and Pb might have been from a different source(s) with Fe. Cd, Cr, Cu, Fe and Pb in BUK 138 environment are probably from the same source while Ni, Mn and Zn might have been from a different source as indicated 139 in Table 4. But in the control area, the BUK C site, Cd, Ni, Mn, Pb were suspected to be from the same source, while Cr, 140 Cu, Fe and Zn might have been from another source. In the overall sites, indicated that Cr and Cu are from the same source while Cd, Cr, Cu, Ni, Mn and Pb are from another source. 141

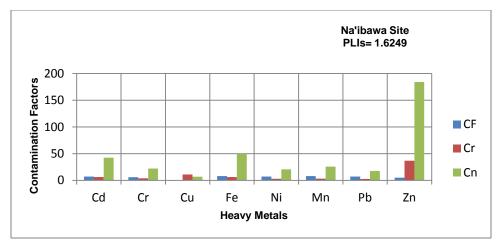
142 **3.3 Pollution Load Index (PLIs)**

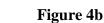
The concentrations of the eight (8) heavy metals for the geological samples were equally computed using equations 5. These computed concentrations were used to obtain the level of pollution within the soil at three different periods (i.e the geological samples were collected before, during, and after planting of the samples) and equations 5 and 6 were used in determining the pollution load index (PLI), and contamination factors (Cf), which were presented in **Figures 4** (Contamination factor Values) and Table 7 (Pollution Load Index Values).

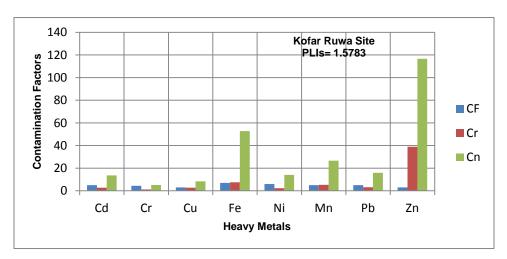
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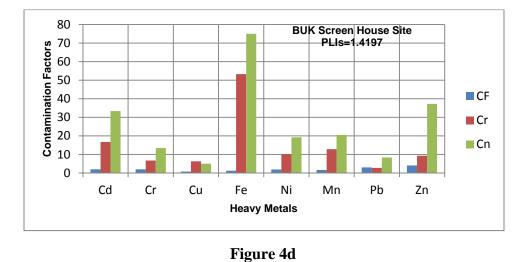


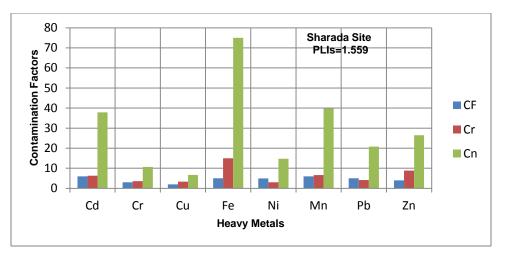












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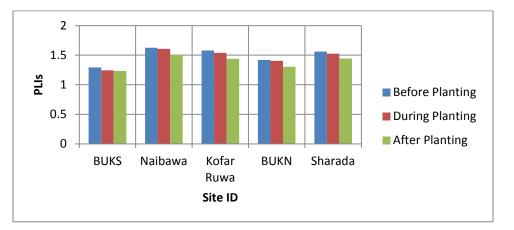
Figure 4e

162 Table 7: Pollution Load Index of Soil (PLIs) Site

PLIs	Before Planting of the Samples	During Planting of the Samples	After Planting of the Samples
BUKS	1.2927	1.2444	1.2318
Naibawa	1.6249	1.6067	1.5098
Kofar Ruwa	1.5783	1.5386	1.4372
BUKN	1.4197	1.4029	1.3028
Sharada	1.5590	1.5253	1.4449

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The values computes in relation to the concentrations (C_n , C_r , and C_f), were used to compute the level of contamination. PLIs was use to indicate at what level is our site place base on the values obtained. According to Ahmed *et al.*, (2014), if the $C_{f < 1}$, indicate low contamination, $1 \le C_f \le 3$; Moderate Contamination, $3 \le C_f \le 6$ and $C_f > 6$; Severe Contamination. While for PLIs: when PLIs < 1; absence of Contamination, PLIs = 1; Low contamination, and PLIs >1; High contamination. Hence using these references and evaluating table 7 in bar chart as given in figure 5.



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170 Figure 5: Bar chart representing contamination levels from the five sites.

171 It can be deduced that the five sites are contaminated with heavy metals. However looking at the different periods in 172 which pollution level varies, one can say that the pollution reduces with time relative to the plantation of the samples. This 173 indicates that the PLIs decreases as the plants grow in the five sites as a result of absorption of the metals by the plants.

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177 **4.0 CONCLUSION**

The soil sample from the site collected contained at least eight (8) heavy metals (Cr, Cd, Cu, Fe, Zn, Ni, Pb, and Mn), with different concentrations in each site.

- 179 different concentrations in each site.
- 180 The correlation between the Heavy Metals was obtained using SPSS 20.0. From the correlation matrix given in **Table 2** 181 **to 5**, it reveals that most probably at Naibawa site (Table 2), Cd, Cr, Cu, Fe, Ni, Mn, and Pb found were from the same
- 182 source, while Zn might have been from another source. At Kofar Ruwa site (table3), Fe and Zn found were probably
- from the same source, while Cd, Cr, Cu, Ni, Mn and Pb might have been from other source. At BUK-N (Table 4), Cd, Cr,
- 184 Cu, Fe and Pb might be from the same source, while Ni, Mn and Zn might be from a different source. At BUK-C (Table
- 5): Cd, Ni, Mn, Pb might have originated from the same source while Cr, Cu, Fe and Zn might be from a different source.
- 186 From the soil and the heavy metals analyses, it was found that the soils are contaminated with the heavy metals.
- 187 The Pollution Load Index computed (PLI) in each site was greater than 1, hence the sites are considered to be
- 188 contaminated.
- 189 From the pollution Load Index computed, before, during, after planting the two samples it is observed that there is
- 190 significant decrease in the level of contamination which could be attributed to some amount of the heavy metals
- absorbed by the samples during plantation of the samples, and if more were planted, the metal level in the soil would
- be reduced drastically.
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