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Analysis of the Pollution Level and Its Variation: A Case Study of Some Selected Sites within Kano State Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Author NFI designed the study and reviewed the draft manuscript. Author UMI conducted the research, analyzed the samples (using AAS), wrote the first draft of the manuscript and wrote the protocol. Author FA managed the literature searches. Authors YYI and BH contributed in the management of the analyses of the study. Authors MS and AB managed the formatting, English grammar and possible scientific definition. All authors read and approved the final manuscript.

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ABSTRACT

Aim: This research investigates the pollution level of heavy metals and their variation in five selected areas in Kano state, Nigeria. The heavy metals investigated are Cadmium (Cd), Chromium (Cr), Manganese (Mn), Zinc (Zn), Lead (Pb), Copper (Cu), Iron (Fe), and Nickel (Ni).
Place and Duration of Study: The area under investigation is found to be associated with various

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activities (e.g. Industrialization, blacksmithing, metal scrap dump site, agriculture etc) for the past 40 years but due to increase in population, it is now a compact (Nucleated) settlement. In agricultural areas, some of the farmers use the polluted water released for their source of irrigation activities. The study covers a period of six months (November 2015 to April 2016), based on the period of activities in the selected sites (e.g. cultivation by the farmers, Industrial activities, Melting, Metal scraps etc).

Methodology: Sample Preparation, Preservation and Digestion- The soil samples are collected for Three Months (February, March and April, 2016) after the sites were prepared for three months (November, December 2015 and January, 2016) for the experiment. Each time the sample was collected it was shade-dried for seven days on the plastic trays to avoid metal contact. The dried samples are grinded using ceramic coating, then sieved into refined powder and leveled into polythene bags, for storage under the ambient temperature [1].

Procedure: A beaker containing 1gm of soil sample and 30ml of Aqua regia (HNO_3 +HCl) at 3:1 ratio was placed into mixer (vibrator) for one hour thirty minutes. Filter paper (Whiteman No.42) was used to filter the solution (suspension) on a separate beaker and distilled water was added to marked 50ml. Atomic absorption spectroscopy ((ASS)$_{\text{-Model 210 VGP}}$) was used to determine the presence and concentration of; Pb, Cd, Ni, Cu, Cr, Zn, Mn and Fe with the corresponding wavelength of each metal; 248.3, 213.9, 232, 357.9, 228.8, 217, 279.5 and 324.8nm respectively. The result obtained was further analyzed using SPSS 20.0.

Results: It is found that in all the five (5) sites (locations) of the study, there exist all the eight heavy metals (HMs) in varying concentrations. The slopes are 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). These values are used to compute the concentration of the eight metals identified, which gave the order of concentrations as: Zn>Ni>Mn>Fe>Cu>Pb>Cr>Cd (for February and March, 2016) but Ni>Cu>Pb>Mn>Fe>Cd>Cr>Zn (For April, 2016). The pollution load index for the five locations is obtained as: 1.2927 (BUK), 1.6249 (Naibawa), 1.6783 (KofarRuwa), 1.4197 (BUK Screen) and 1.559 (Sharada).

Conclusion: The results obtained reveals that eight (8) HMs are determined - (Cr, Cd, Cu, Fe, Zn, Ni, Pb, and Mn). These HMs recorded different/varying concentrations (within the soil). The correlation matrix generated from the concentrations of samples obtained shows that in each site, there is group of HMs that originate from the same source(s) and others that emanate from another source (s). In Naibawa, Cd, Cr, Cu, Fe, Ni, Mn, and Pbhave high probability of originating from the same source while Zn might have originated from a different source But in *KofarRuwa site*, Fe and Zn recorded high probability of originating from the same source while Cd, Cr, Cu, Ni, Mn and Pb are from other source(s). In BUK – E; Cd, Cr, Cu, Fe and Pb are probably from the same source, while Ni, Mn and Znare from different source. In the control area (BUK C site), Cd, Ni, Mn, Pb recorded values have probabilities, indicating they are from the same source while Cr, Cu, Fe and Zn are contrary from the latter. In the overall sites, the data generated reveals 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 indicates decrease in the level of contamination in all the sites.

Keywords: AAS; heavy metals; phythoremediator; sunflower and vegetable.

1. INTRODUCTION

Several efforts are made towards safeguarding the health of the society by conducting researches on the composition of samples using various techniques. These researchers range from identification, determination, study and evaluation of samples (Biological and geological). Natasa et al. [2] reports that; Melting operation, sludge dumping, intensive agriculture, traffic activities, power transmission, cement – pollution and smelting are possible ways of heavy metal accumulation [2]. Metal Contamination in agricultural soil is of increasing concern, due to food safety issues and potential health risk [3]. Heavy Metal (HMs) pollution has pervaded many parts of the developing countries and affects humans because of their longevity and accumulation in their organs via different ways [4,5]. The non-biodegradability of HMs and their potential to cause inappropriate effect made them the most noxious material [6]. It is widely reported that they have both positive and negative role in human life. The elements play important role in the biological process, but at high concentrations they may be toxic to biota, disturb the biochemical process and cause hazards. Excessive content of HMs beyond maximum permissible level (MPL) leads to number of nervous, cardiovascular, renal, neurological impairment as well as bone diseases, which significantly contribute to decrease human life expectancy (9-10 years), within the affected area and several other health disorders [3]. In 2008, Khan et al. [7] reports that National Research Council (NRC) has outlined four steps (processes) in estimating health risk agent, which are hazard identification, exposure assessment, dose/response assessment, and risk characterization. This problem is not an exception in Nigeria as Ahmed et al. reports that the risk level Nigerians and other African countries are exposed to [8]. Their search scope is 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 8°20'W and 8°27'E of meridian, as presented in Fig. 1.

The study areas are found to be an industrial area for the past 40 years but due to the increase in population, the areas are now a compacted (Nucleated) settlement. Also some of the peopleuse the water released from the industries for their irrigation activities.

The study is aims at determining the level of concentration of HMs (as Pollutants) in some selected area in Kano state due to the increased in population, industrial activities (effluent), metal scraps, agricultural activities, provided possible solution and the to call the attention of the authority to come to the aid of the residents. The specific objective of the study is identifying the HMs in these areas, finding out whether the metals comes from the same source or not and at what level of concentration are they placed and determining the level of contamination in the selected areas.

1.1 Theoretical Background

One of the governing equations that gives a relationship between, α (the analyte's absorptivity with units of $cm^{-1}conc^{-1}$); Concentration, C; Absorbance, A; and width, b; is the Beer's law (some time called Beer – Lambert Law), as presented in equation (1):

$$A = \alpha b C \quad (1)$$

When expressing the concentration using molarity, then *α* will be replaced with the molar absorptivity,ε, which has unit of cm^{-1} M^{-1}. Hence:

$$A = \varepsilon b C \quad (2)$$

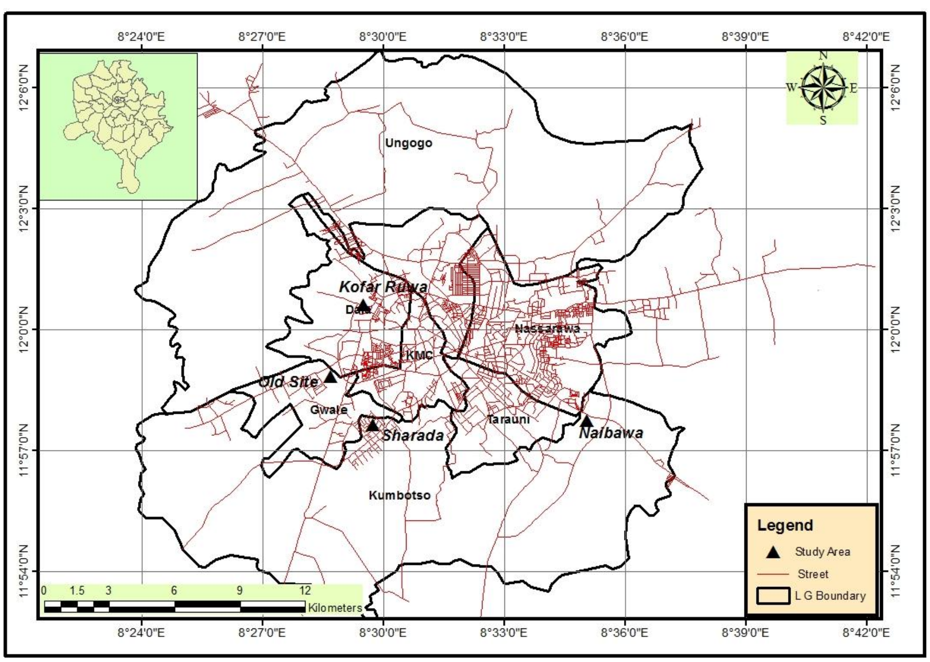

Fig. 1. The five (5) selected sample site: Sharada, Kofa Ruwa, Naibawa and Bayero University (two locations) Kano

The concentration of HMs is directly related to the absorbance of the metals by a substance. In this research work we are interested in the Soil Samples Concentration (C_{sample}), and Pollution Load Index (PLIs). In order to have the concentrations of these metals, the equations used by Udo*et al.* and Cui *et al.,* were employed [9,10].

$$C_1V_1 = C_2V_2 \quad (3)$$

Where C_n is the concentration of solution and V_n is the volume (for n=1,2,3,…,n).

Concentration of sample (C_{sample})

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

where Abs. is Reading of absorbance (with respect to Heavy Metals) [1,8,11].

Pollution Load Index Soil (PLIs)

Ahmed et al. [11] reported methods used in indicating the level of contamination of soil ranging from low, moderate and severe contamination. The equations are given as:

$$C_f = \frac{C_n}{C_r} \quad (5)$$

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 [12,13]:

$$PLIs = \sqrt[n]{C_{f1} + C_{f2} + C_{f3} + \ldots + C_{fn}} \quad (6)$$

2. MATERIALS AND METHODS

Five (5) experimental sites are set up within Kano State, Nigeria. These are: (a) Bayero University, Kano Screen House (BUK-C) – 8°28'0" E & 11°59'0" N, (b) Bayero University, Kano Environment (BUK-E) – 8°28'0" E & 11°59'0" N (c) KofarRuwa (K) – 8°29' 5" E & 12°1' 5" N,(d) Naibawa (N) – 8°35'0" E & 11°58'0"N and (e) Sharada (S)- 8°29'5"E & 11°58'0"N. as shown in Fig. 1.

2.1 Sample Preparation, Preservation and Digestion

The soil samples are collected for Three Months (February, March and April, 2016) after the sites were prepared (before, during and after plantations) for three months (November, December and January, 2015). Each time the sample were collected it was shade-dried for seven days on the plastic trays to avoid metal contact. The dried samples are grinded using ceramic coating, then sieved into refined powder and leveled into polythene bags, for storage under the ambient temperature [1].

2.2 Procedure

A beaker containing 1 gm of soil sample and 30 ml of Aqua regia (HNO_3 +HCl) at 3:1 ratio is placed into mixer (vibrator) for one hour thirty minutes. Filter paper (Whiteman No.42) is used to filter the solution (suspension) on a separate beaker and distilled water is added to marked 50 ml. Atomic absorption spectroscopy ($(ASS)_{-Model\ 210\ VGP}$) is used to determine the presence and concentration of; Pb, Cd, Ni, Cu, Cr, Zn, Mn and Fe with the corresponding wavelength of each metal; 248.3, 213.9, 232, 357.9, 228.8, 217, 279.5 and 324.8 nm respectively. The result obtained was further analyzed using SPSS 20.0.

2.2 Statistical Method

SPSS 20.0 version was employed to analyze the concentrations of the eight heavy metals determined. Regression analysis is also used to obtain the slope values that are used to compute the concentrations. The correlation matrix was equally generated and the heavy metals are identified and discussed to be from the same or different source(s). The correlation is in term of probabilities with a heavy metal selected as it reference base on the activities in the area.

3. RESULTS AND DISCUSSION

3.1 Samples Concentrations

The concentration of heavy metals is directly related to the absorbance of metals by the samples [14], equation (3) was used to calculate the concentrations of metals in the sample. The standard/slope was computed using equation (4). Different volumes of solutions at different concentrations are prepared and analyzed using AAS machine to obtain the absorbance. The concentration and absorbance of each metal are given in Table 1.

The values of the concentration for these heavy metals (HMs), in the soil samples were analyze in five different sites. In determining the concentration (in the soil samples) of the HMs, various solution (with different volume) and varying concentration and its equivalent absorbance was produced using Atomic Absorbance Spectroscopy (AAS), The values of absorbance and concentrations are tabulated in Table 1. Using the same Table 1, slopes of these HMs 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). The computed values of the slope reveal that the concentrations are directly proportional to the absorbance. Using equation (4) the concentrations were generated and presented in Fig. 2.

Table 1. Cd, Cr, Cu Fe, Ni, Mn, Pb, and Zn concentration (mg/kg) and absorbance values

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
Chromium(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
Copper(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
Iron(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
Nickle (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
Manganese(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
Lead(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
Zinc(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

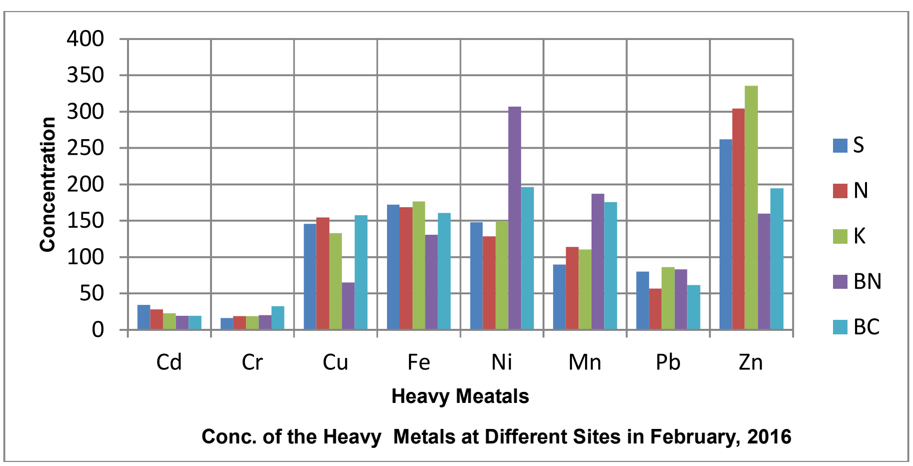

Fig. 2a. Comparison of heavy metals from different sites base on their concentrations in February 2016

Fig. 2a reported the concentration of each HMs with respect to their sites. In February 2016, all the HMs studied Zn and Ni recorded the highest values, followed by Fe, Mn, Cu, Pb, Cr and Cd.

In Fig. 2b, the same HMs were presented for the month of March 2016, where it was observed that there are general decrease in the concentrations of the HMs when compared with the concentrations of these metals in the months of February 2016. By extension there are changes in the conditions of the sites (soils).

As for the month of April 2016, (Given in Fig. 2c), similar behavior as recorded in the previous month (March, 2016) was significantly seen, this is connected to the common activities in the sites (farming) as reported, [1,15]. However Cu and Zn appear to have the highest concentrations when compared with the other HMs.

Fig. 3, gave all the concentrations of the eight (8) HMs in different sites and their comparison base on Months and metals. From it, **Ni** records the highest concentration and **Cd** has the least. Overall the concentration base on monthly basis ascends from February, March, and then April 2016.

3.2 Correlation of the Eight Heavy Metals

To investigate the correlations between the metals, SPSS 20.0 was used and the result obtained was tabulated in Tables 2, 3, 4, 5, and 6.

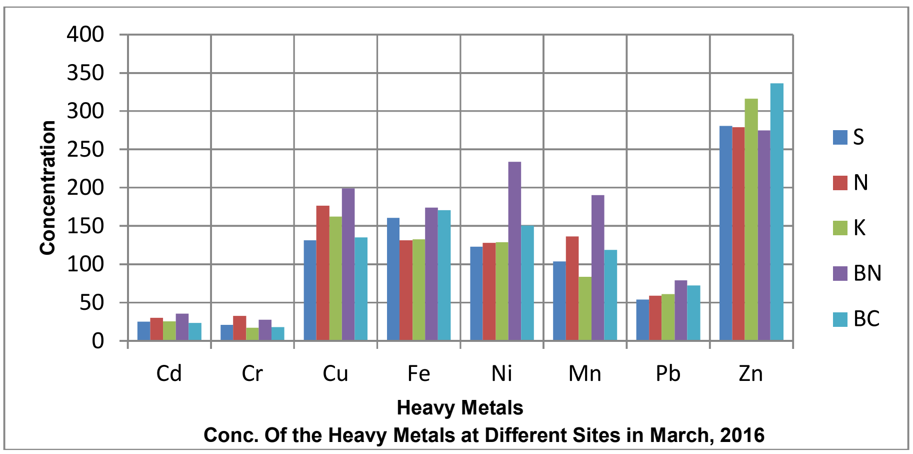

Fig. 2b. Comparison of heavy metals from different sites base on their concentrations in March

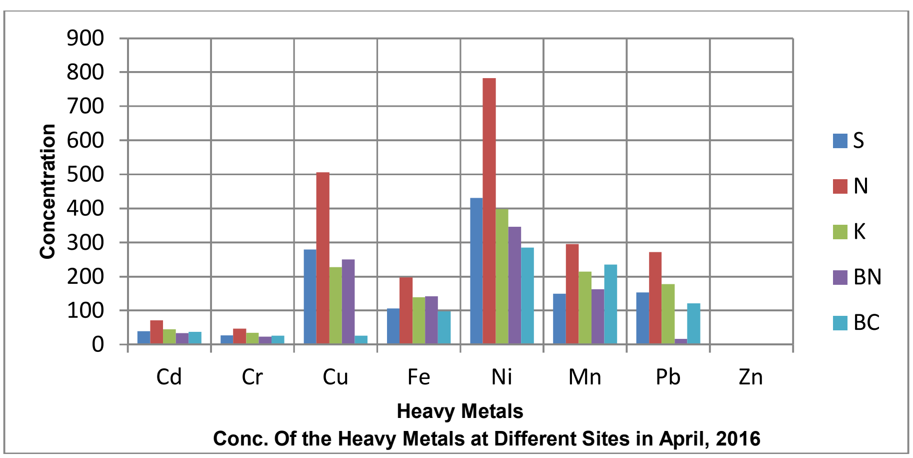

Fig. 2c. Comparison of heavy metals from different sites base on their concentrations in April

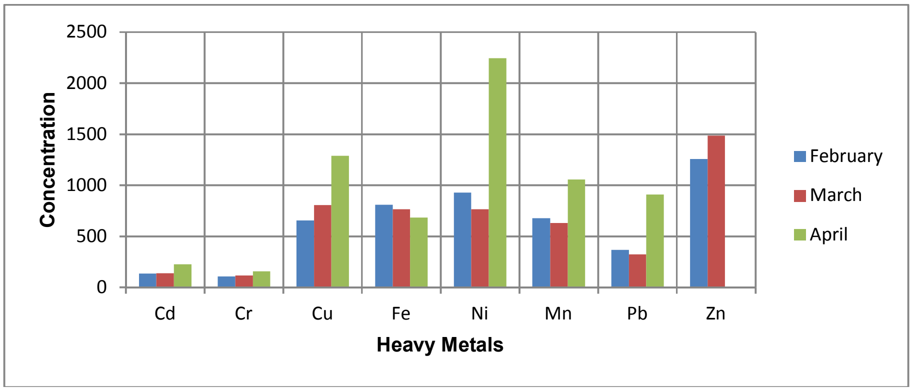

Fig. 3. Total concentration of the heavy metals for three months (February, March and April, 2016)

Table 2.Correlation matrix of the heavy metals from Naibawa site

	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

From Table 2, it was observe that there is highest probability that Cd, Cr, Cu Fe, Ni, Mn, and Pb are from the same source(s), while Zinc originate from a different source(s). This was expected considering the nature of the site (Dump site).

Table 3, reported the correlation probabilities of the HMs at KofarRuwa market (Iron scraps). It was found that Cd, Cr and Cu originate from the same source(s). Fe, Ni, Mn, Pb and Znstands alone with a unitaryprobability but variable probabilities when compared to the other HMs in the sites. However looking at the nature the site this results is expected.

In Table 4, the probability shows that Cd, Cr, Cu, Fe and Pb are produced from the same sources while Ni, Mn, and Zn were produced from a different source(s).

The probabilities in Table 5, report that Cd, Ni, Mn and Pb are produced from the same source while Cr, Cu, Fe, and Zn have been from another source(s).

Table 6 shows the overall summary of the correlation between the metals studies. It was found that Cu and Cr are produced from the same source in all the locations while Cd, Ni, Mn, Zn and Pb are produced from different sources.

Table 3. Correlation matrix of the heavy metals from KofarRuwa site

	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

Table 4. Correlation matrix of the heavy metals for BUK environs site

	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

Table 5. Correlation matrix of the heavy metals for BUK screen house site

	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

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

3.3 Pollution Load Index (PLIs)

Pollution load Index (PLIs) is another way used to determine the level of pollution in a given sample (soil). Three (3) factors were studied, using the concentrations of the eight HMs (geological samples) computed using equations (4). These factors are Concentration of soil (C_n), Background Concentration (C_r) and Contamination factor (C_f) using equations 5 and 6. These factors were then employed in computing the PLIs and presented in Figs. 4a, 4b, 4c, 4d and 4e.

Fig. 4a shows that there is high contamination factor of the HMs, with Ni, recording the highest, their by decreasing in the following sequence Fe, Mn, Zn, Cd, Pb, Cu, and Cr in BUK site with PLIs value of 1.2927.

In Naibawa it was found that Zn recorded the highest contamination value in the soil followed by Fe, Cd, Mn, Cr, Ni, Cu and Pb with PLIs value of 1.6249 as presented in Fig. 4b.

Similarly Zn, Fe, Mn, Ni, Pb, Cd, Ni, and Cu are the order of the level of contamination (by HMs) in KofarRuwa site. The PLIs computed in this site is 1.6783 as presented in Fig. 4c.

In the control site (BUK Screen House) the contamination is relatively low compare to the background and concentration of the HMs. However, the PLIs was obtained to be 1.4197. The HMs contamination factor level decrease in sequence Zn, Cd, Mn, Ni, Cr, Pb, and Cu, this is presented in Fig. 4d.

The PLIs value is 1.559 in Sharada with Fe recording the highest contamination factor then followed by Mn, Cd, Zn, Pb, Ni, Cr, and Cu.

Considering Figs. 4a to 4e, the computed contamination factors are all greater than 1 [16,17], this means that the sites are contaminated.

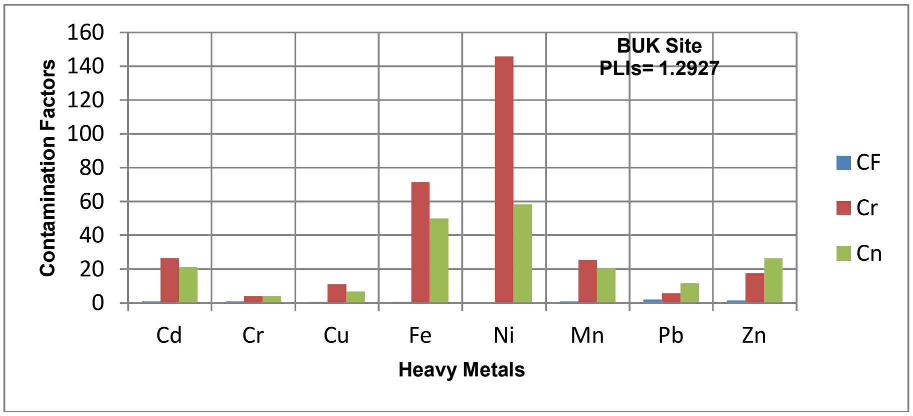

Fig. 4a. Barchart indicating BUK site contamination level and the value of PLIs (1.2927)

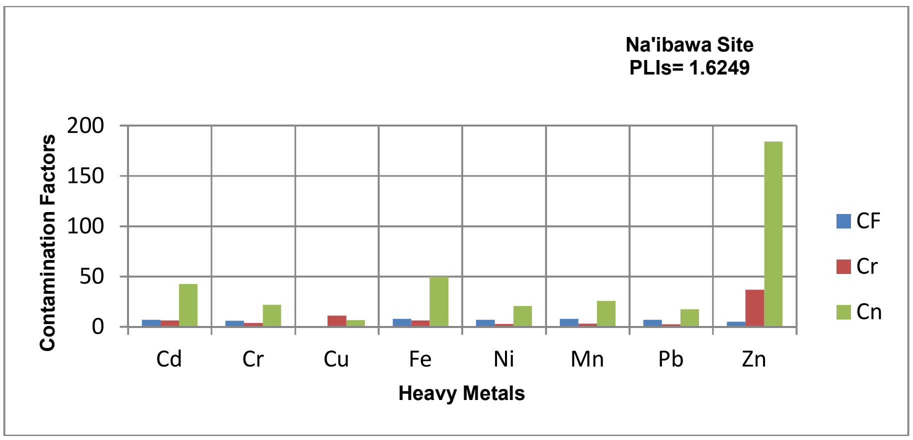

Fig. 4b. Barchart indicating Naibawa site contamination level and the value of PLIs (1.6249)

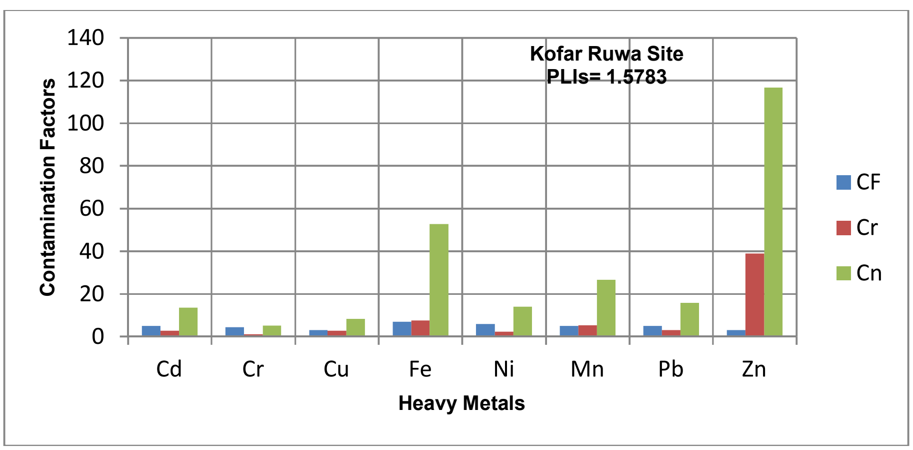

Fig. 4c. Barchart indicating KofarRuwa site contamination level and the value of PLIs (1.6783)

The level of contamination of the soil (sites) was analyze in three phase. The first phase is before plantation (farming), i.e the three months preparation for cultivation, then the second phase is during the plantations and thelast phase is after the plantations. In each period the samples were collected and the PLIs was determined. Table 7 gave the tabulated readings for the three periods for each sites. The values compute in relation to the concentrations (C_n, C_r, and C_f), are used to compute the level of contamination. PLIs is use to indicate at what level is our site place base on the values obtained. According to researches, if the $C_{f<}$ 1, indicates low contamination, $1 \leq C_f \leq 3$; Moderate Contamination, $3 \leq C_f \leq 6$ and $C_f > 6$; Severe Contamination. While for PLIs: when PLIs < 1; absence of Contamination, PLIs = 1; Low contamination, and PLIs >1; High contamination [18,19,20,12]. Fig. 5 show the representation of Table 7 in form of a bar chart.

It can be deduced that the five sites are contaminated with HMs. However looking at the different periods in which pollution level varies, one can say that the pollution reduces with a time relative to the plantation of the samples. As reported [1], the declining (decreasing)

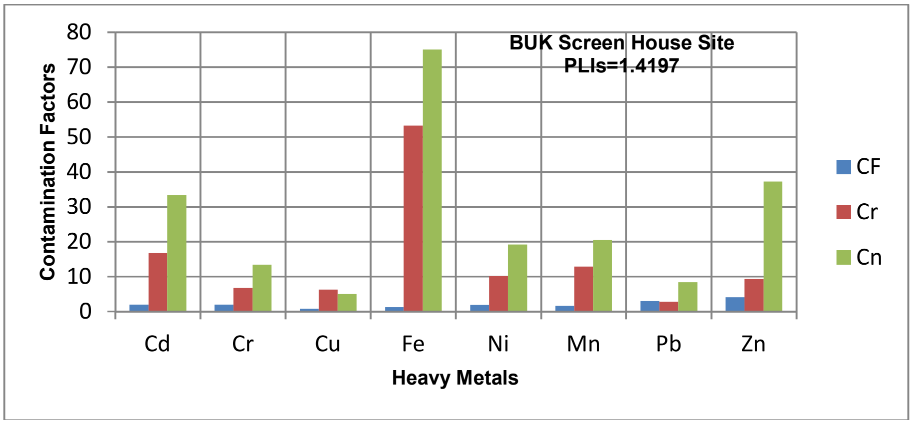

Fig. 4d. Bar chart indicating BUK Screen House site contamination level and the value of PLIs (1.4197)

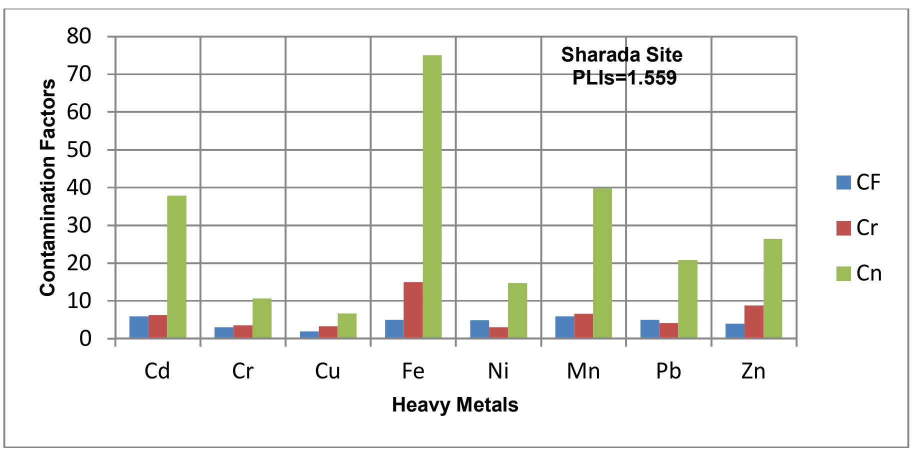

Fig. 4e. Barchart indicating Sharada site contamination level and the value of PLIs (1.559)

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
KofarRuwa	1.5783	1.5386	1.4372
BUKN	1.4197	1.4029	1.3028
Sharada	1.5590	1.5253	1.4449

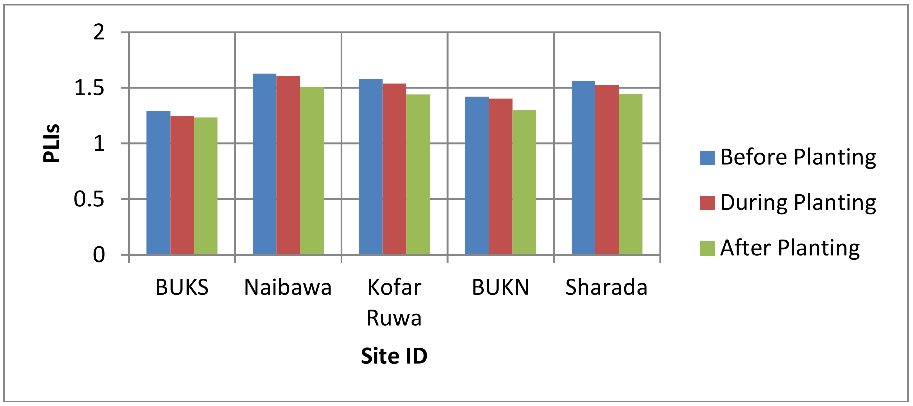

Fig. 5. Bar chart representing contamination levels from the five sites

values in this report indicate that the PLIs decreases as the plants grow in the five sites as a result of absorption of the metals by the plants.

4. CONCLUSION

The concentrations of eight (8) HMs (Cr, Cd, Cu, Fe, Zn, Ni, Pb, and Mn) are determined. These heavy metals recorded different/varying concentrations, within the soil and the plant's samples.

The correlation matrix generated from the concentrations of samples obtained reveals that in each site, there are group of HMs that originate from the same source(s) and others that emanate from the other source(s).

The Pollution Load Index computed (PLI) in each site is greater than 1, hence the sites are considered to be contaminated. However the pollution Load Index computed, before, during, after planting of the two samples, it shows that there is significant decrease in the level of contamination which could be attributed to some amount of the HMs absorbed by the samples during plantation of the samples, and if more are planted, the metal level in the soil would be reduced drastically.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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