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Assessment of Heavy Metal Pollution on Roadside Dusts from Selected Locations in Ilorin, Nigeria Using AAS Techniques.

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ABSTRACT

This study investigated the concentration of four priority heavy metals on the roadside dusts of selected areas in Ilorin, Kwara State, Nigeria. Thirty composite dust samples were collected along ten different roadsides and these were based on distances from the roads. The seasonal variation of metals due to their different locations was determined. The metal analysis was carried out with the aid of atomic absorption spectroscopy (AAS). Metal concentrations in the roadside dust followed the order of Zn> Pb> Cu > Cd. Accumulation of heavy metals in dust was greatly influenced by traffic volume and exhaust from motor vehicles. Other sources such as battery wastes, car tyres, presence of iron benders, welders and indiscriminate dumping of refuse on the roadside might also contribute significantly to the metal pollution. However, the paper suggested a regular monitory and assessment to ensure sustainable management of the environment.

KEYWORDS: Heavy metals; Roadside dusts; Concentration; Ilorin; Pollution.

Introduction

Heavy metal contamination in urban street dust has become a growing concern in recent years. A recent survey of heavy metals on roadside dusts (Malsingh, 1999) has shown that lead, copper and zinc are consistently present. The major source of lead, along local roadways, is leaded gasoline combustion products in automobile exhaust emissions. On the other hand, copper appears to originate from electricity and telephone cables, while zinc is likely to be from galvanized iron sheets that are used on the roofs of most buildings. Urban surfaces receive deposits from various sources such as vehicle emissions, industrial discharges, domestic heating, waste incineration and other anthropogenic activities through atmospheric transport as well as from human activities (Gibson and Farmer, 1986; Okoro et al., 2012; Okoro et al., 2013; Okoro et al., 2014a; Okoro et al., 2014b; Okoro et al., 2016; Okoro et al., 2017). Street dusts and top roadside soils in human areas are indicators of heavy metal contamination from atmospheric deposition.

The source of heavy metals like Pb could be from leaded gasoline, Cu, Zn, and Cd from car components, tyre abrasion, lubricants, industrial and incinerator emissions (Markus *et al.*, 1996). The source of Ni and Cr in street dust is believed to be corrosion of cars and chrome plating of some motor vehicle parts (Al-Shayep and Seaward, 2001).Road side dust investigation is of particular importance here for two main reasons. Firstly, roadside dust is freely being inhaled by those traversing the streets and those residing within the vicinity of the streets. The more the dusts on such streets become contaminated with heavy metals, the more such people are exposed to the health hazards associated with such metals.

Secondly, the street dust is one of the major media through which heavy metals may find their ways to the soil and surface and underground water through rains and subsequently living tissues of plants, animals and human beings. Also in recent years, there is growing concern for the potential contribution of ingested dust to metal toxicity in humans (Chirenje *et al.*, 2006). Young children are more likely to ingest significant quantities of dust than adults because of the behaviour of mouthing non-food objects and repetitive hand/ finger sucking (Bargali, 1998). Besides, children have a much higher absorption rate of heavy metals from digestion system and higher haemoglobin sensitivity to heavy metals than adults (Hammond, 1982).

Road traffic is one of the most important sources of pollution in urban centres and roadsides. The increase in private vehicle traffic has masked the reduction of emission rate. We are now confronted with the appearance and emergence of other pollutants, produced as a result of abrasion with dare consequences of public health by contact, inhalation or consumption of contaminated products (Gebel *et al.*, 1997; Benes and Grieken, 2004). The objective of this research is to investigate heavy metal pollution level of road side dust from selected locations in Ilorin environment using AAS techniques.

Materials and Methods

Study area

Kwara State lies between the sedimentary belt of north, central region of Nigeria; Ilorin is a major industrial and commercial hub with a large population of about 3 millions. The selected areas for this investigation were areas with high traffic and business activities (Fig.1). These areas are always busy within the hours of 6:30am to 9:00am when offices and commercial activities commenced and 4:00pm to 7:30pm in the evening at the close of work or market activities. The location considered for this analysis is around the University campus and Challenge area.Ten major sampling sites were randomly selected and labelled (A-J) with an average distance of 50meters from one another. Site A, which is from University Road to site J, which is Pipeline Road, has structure like petroleum dispensing station, runoff from gutters, shops and boutiques who regularly use generators, mechanical and other gasoline powered equipment.

Sample Collections

Dust samples were collected from ten different areas along notable major roads within Ilorin. Three samples were collected from each location at the extreme edges of the roads between February and May 2014. Samples were collected with the plastic container that has been washed with distilled water and dried. They were labelled immediately at the point of collection for proper identification. Each sample was sieved through a sieve of 250 µm diameter.

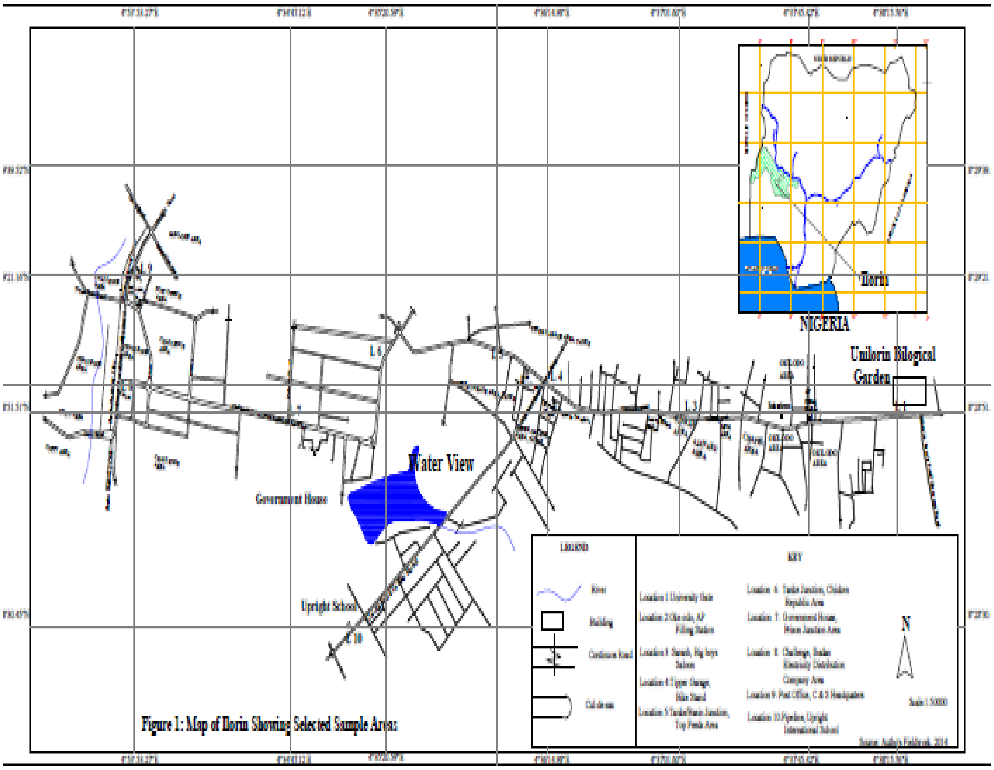

Figure 1: Thestudy area showing some selected locations in Ilorin

Sample Treatment

The reagents used were of good analytical grade. All the standard solution (1000ppm) for Zn, Pb, Cu and Cd was certified. All the glassware and plastic vessels were soaked with dilute nitric acid for 24 hrs and rinsed with distilled water. The samples were gently grinded, dried at 60˚C for 3 days to a constant mass, and then sieved through a 0.25mm stainless steel. 0.5g dried and sieved sample each was transferred into a clean 50 ml volumetric flask for digestion and the sample was digested by adding 10ml 65% HNO_3 and 2 ml concentrated HF. It was heated to dryness on a water bath. 10 ml of 1% HNO_3 was added and heated to boiling point and the solution was allowed to cool. It was finally made up to the mark (Ogunsola *et al.,* 1995). The digested samples were analysed using ALPHA 4 atomic absorption spectrophotometer (Chem-Tech Analytical)

Results and Discussion

The concentration of metals and the contamination ratios in street dust samples of various locations in Ilorin metropolis were presented in (Tables 1). Mean content can be ranked by abundance in the street dusts of all the sampling categories as Location 9 > Location 7 > Location 4 > Location 1 > Location 8 > Location 6> others. The decrease in order of metal abundance from the places of higher activities to the place of lower activities may probably be due to the decrease in vehicle emissions, traffic density and other related issues. The concentration levels of copper, zinc, cadmium, lead were measured in the dust samples collected from the specific locations as shown in Table 1.

Table 1. Concentration levels of heavy metals (mg/L) in the street dust samples from various areas of Ilorin metropolitan city during dry season (Mean ± SD)

Locations	Cu (mg/L)	Zn (mg/L)	Cd (mg/L)	Pb (mg/L)
A	0.31 ± 0.03	1.32 ± 0.21	BDL	0.74 ± 0.20
B	0.19 ± 0.08	0.57 ± 0.26	BDL	0.37 ± 0.17
C	0.32 ± 0.04	1.12 ± 0.19	BDL	0.62 ± 0.01
D	0.21 ± 0.04	1.65 ± 0.09	BDL	0.57 ± 0.12
E	0.19 ± 0.04	0.69 ± 0.24	BDL	0.44 ± 0.07
F	0.31 ± 0.06	1.18 ± 0.43	BDL	0.36 ± 0.12
G	0.54 ± 0.06	3.69 ± 1.39	BDL	0.71 ± 0.07
H	0.28 ± 0.04	1.28 ± 0.31	BDL	0.57 ± 0.09
I	0.43 ± 0.15	4.83 ± 2.40	BDL	1.38 ± 0.96
J	0.30 ± 0.02	0.96 ± 0.01	BDL	0.72 ± 0.01

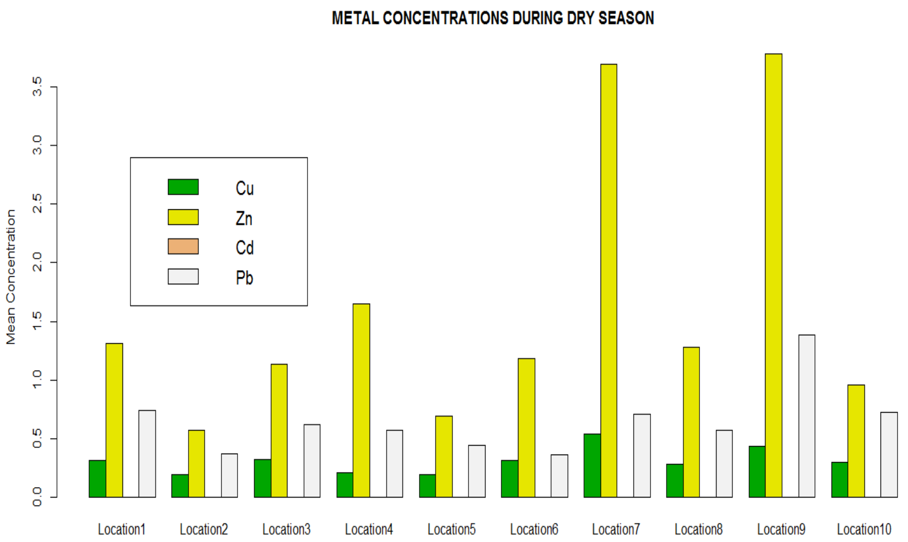

Figure. 2: The concentration of Zn, Pb, Cu, and Cd in the dust samples collected along selected locations in Ilorin during the dry season.

From the results shown in Fig. 2, high level of zinc (ranging from 0.57mg/l to 4.83mg/l) was recorded in all the samples collected in the dry season. Location 9 &7 had the highest concentrationsof zinc. These locations experiencedhigh volume of traffic.Zinc concentrations affect the life of ecosystems, which as a result disturb the food chain, animal diversity and environmental beauty. The level of the zinc metal in this study is in agreement with that ofChirika and Pawan(2011). They assessed the heavy metals in the street dust of Kathmandu metropolitan city where zinc content was found in high concentration and followed by lead.

Lead concentrations in this studyalso ranged from 0.36mg/l to 1.38mg/l in all the locations. But location 9 recorded the highest concentration. Bada and Oyegbami., 2012, observed that all the four metals (Pb, Zn, Cd and Ni) that were determined in the roadside dust of different traffic density in Sapon Road Abeokuta, lead has the highest concentration followed by Zn and Cd. These values indicated that lead fuel could be the potential source of lead contamination in the dust samples. Pb emissions could also be produced from break wear and loss of Pb from wheel can also be the main sources of lead pollution in the urban environment in addition to leaded gasoline (Smichowski *et al.*, 2008).

Also, the distribution of copper along the sampling sites ranged from0.19mg/l to 0.54mg/l. Copper was found to be high in location 7 and low in location 5. Baba et al.(2009) determined the trace metals concentration in roadside dust of Ilorin town. From their findings, the result of copper ranged from 0- 6.8mg/l. Natural sources include decaying vegetation, forest fan, sea sprays and dust storms (Faiz*et al.*, 2009) Release of Cu by human activities includes mining, metal production, sludge deposition, combustion of fossil, wood production and phosphate fertilizer production. Cadmium exhibited significantly low levels in all the samples compared with the findings of Faiz*et al.*,(2009) who concluded that the street dust generally contained lower levels of Cd.

Table 2: Concentration levels of heavy metals (mg/l)in street dust samples from various areas of Ilorin metropolitan city during the wet season. (Mean ± SD)

Sample Code	Cu (mg/l)	Zn (mg/l)	Cd (mg/l)	Pb (mg/l)
A	0.166±0.00	0.743±0.114	0.003±0.004	0.50±0.061
B	0.133±0.01	0.833±0.084	0.01±0.008	0.41±0.11
C	0.25±0.032	0.523±0.061	BDL	0.33±0.014
D	0.32±0.080	1.813±0.604	BDL	0.626±0.028
E	0.18±0.069	1.03± 0.404	BDL	0.306±0.062
F	0.473±0.04	1.5 ± 0.057	BDL	0.87 ± 0.106
G	0.336±0.02	2.506±0.138	BDL	0.576±0.074
H	0.466±0.00	1.696±0.036	BDL	0.536± 0.074
I	0.51±0.208	2.51±1.093	BDL	0.613±0.051
J	0.273±0.03	0.853±0.030	BDL	0.6 ± 0.016

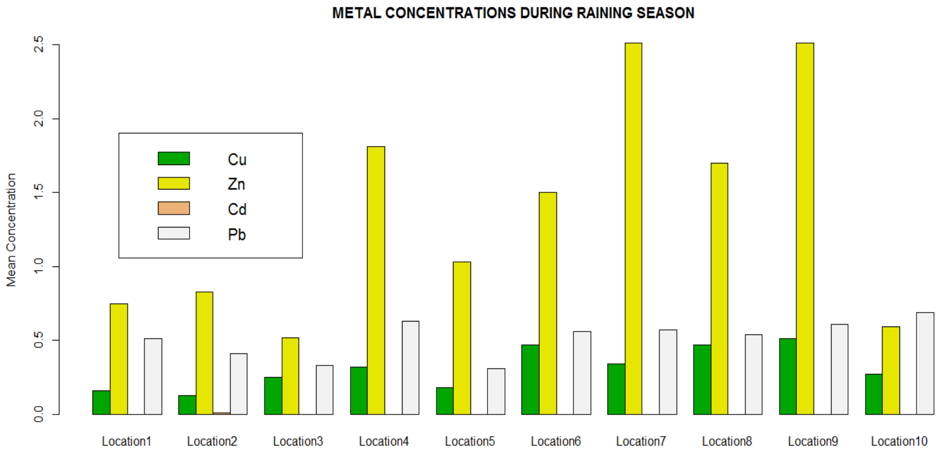

Figure 3: The concentration of Zn, Pb, Cu, and Cd in the dust samples collected along selected locations in Ilorin during the wet season.

Fig. 3 above showed the concentration of heavy metals during the wetseason. Highconcentration levels of zinc were recorded (location 9 & 7) in all the samples collected followed by lead and copper. It was observed here that trace of cadmium was found in the sample collected from the roadside dust during the wet season.

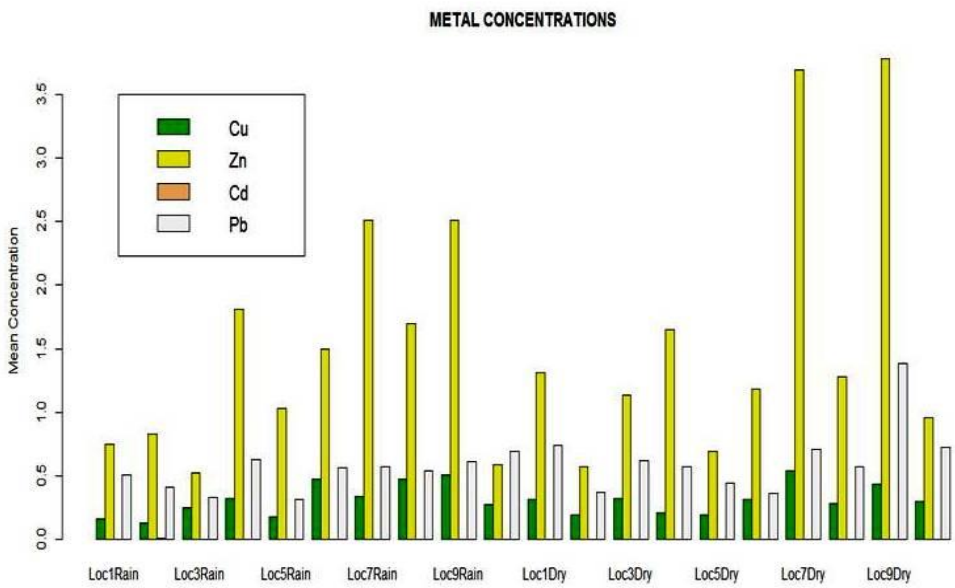

Figure 4: The concentration of Zn, Pb, Cu, and Cd in the dust samples collected along selected locations in Ilorin for both wet season and dry season.

Fig. 4showed the concentration of heavy metals at various locations sampled during the two seasons (wet and dry) and it indicates the effect of the metals at seasonal variation due to collection been made at different locations. Generally, under the variations we can simply say that zinc is observed to have the highest concentration followed by lead and copper in all the seasons but cadmium was not found.Copper has almost the same concentration in both the seasons.Therefore, it was observed that dry weather condition may increase the heavy metal concentration due to the bigger particles size of the dust than the wet season and this might be as a result of washing away of the metalsduring raining season.

Statistical Analysis

In order to establish inter-metal relationships in the samples, correlation coefficient of the metals at the ten sampling road for each season was carried out in Table (3)

Table 3: The Inter-element correlation for dry season

	Copper (Cu)	Zinc (Zn)	Lead (Pb)
Copper (Cu)	1	0.866	0.590
Zinc (Zn)		1	0.751
Lead (Pb)			1

There is a positive relationship between all the metals during the dry season. The correlations between Cu-Zn, Zn-Pb which is r=0.866 and r= 0.751 respectively indicate there is positive relationship between the metals which is showing a signal that the pair of metals are from the same source (i.e. the body parts and tires of automobiles as well as vehicular emissions). The relationship indicates the interdependence of these metal pairs. There was no positive relationship between cadmium and other metals (r= 0.000) because Cd was not found in the dust sample been analysed. The relationship between Cu-Pb is observed to be r=0.59, which shows that the two metals belong to the same natural or manmade source of emission that is they are going in the same direction in such a way that when there is increase in the concentration of copper there is also an increase in the concentration of zinc, if Cu increases the concentration of Pb increases because they still maintain a positive relationship.

Table 4: The Inter-element correlations for rain season

Elements	Copper (Cu)	Zinc (Zn)	Cadmium (Cd)	Lead (Pb)
Copper (Cu)	1	0.711	–0.461	0.531
Zinc (Zn)		1	–0.256	0.450
Cadmium (Cd)			1	–0.293
Lead (Pb)				1

There is a positive relationship between Cu–Zn, Cu–Pb, and Zn–Pb, while we have a negative relationship between Cu–Cd, Zn–Cd and Cd–Pb. In the correlation of the wet season, there is a positive relationship between Cu- Zn, which is observed to be r= 0.71, Cu- Pb, which is r=0.531 and Zn- Pb is observed to be r=0.45 just as it was noticed in the dry season. But for the one having negative sign, it means we have a negative relationship between the metals which are Cu-Cd, having a correlation of r= -0.46, Zn- Cd also having r= -0.25, then Cd- Pd having a correlation of r= 0.29. Though it is as a result of their relationship with the concentration of cadmium, a low concentration of cadmium was found during the wet season in the dust samples of some of the locations which gives a poor correlation, it can also be stated that the two metals involved are from different sources that is the metals have different independent source.

Table 5: The Pearson correlation between Metals

		Correlations			
		Copper	Zinc	Cadmium	Lead
Copper	Pearson Correlation	1	0.747**	-.349	0.478*
	Sig. (2-tailed)		0.000	.131	0.033
	N	20	20	20	20
Zinc	Pearson Correlation	0.747**	1	-.165	0.679**
	Sig. (2-tailed)	0.000		.487	0.001
	N	20	20	20	20
Cadmium	Pearson Correlation	-0.349	-0.165	1	-0.176
	Sig. (2-tailed)	0.131	0.487		0.457
	N	20	20	20	20
Lead	Pearson Correlation	.478*	.679**	-.176	1
	Sig. (2-tailed)	.033	.001	.457	
	N	20	20	20	20

Table 6: Total Variance Explained Extraction Method: Principal Component Analysis.

	Initial Eigen values			Extraction Sums of Squared Loadings		
Component	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	2.390	59.745	59.745	2.390	59.2+6745	59.745
2	.928	23.202	82.947			
3	.502	12.557	95.505			
4	.180	4.495	100.000			

The association of the heavy elements with each other was studied through the Pearson correlation coefficient R given in Table 6. The negative or small values of R indicate the independent sources of the elements, whereas the large positive values of R show the association of the elements with one another. The 0.74 and 0.47 values of R between Cu and Zn, Cu and Pb depict the common source of these elements. The strong correlation of the elements indicates that both the elements may have common anthropogenic or natural sources.

The manmade activities include burning of coal as well as waste disposals in the surroundings; however the natural source may include the dust particles. This shows the total variance, result gotten from the Initial Eigen values and the Extraction sums.

Principal component analysis (PCA) is a statistical technique used to examine the interrelations among set of variables in order to identify the underlying structure of those variables. The number of variables determines the number of components that principal component analysis (PCA) will create. That is, since four variables were gotten, definitely, we would be expecting four components. (PCA) will list the components in the order of their variance (Eigen values), the first component will have the greatest Eigen value or variance which is 2.390 from the table, followed by the second greatest variance which is 0.928 and the third variance which is 0.502.

Methods of determining the number of components to retain.

- Eigen value
- Screen test or screen plot

Under initial Eigen value since the first value which is 2.390 is greater than one, the component was retained which is component one. The Eigen value for the second component is less than 1, the component is not retained. The same principle goes to component 3&4. That is what extraction sums of squared loading is explaining because only component 1 was retained due to its Eigen value that is greater than 1.

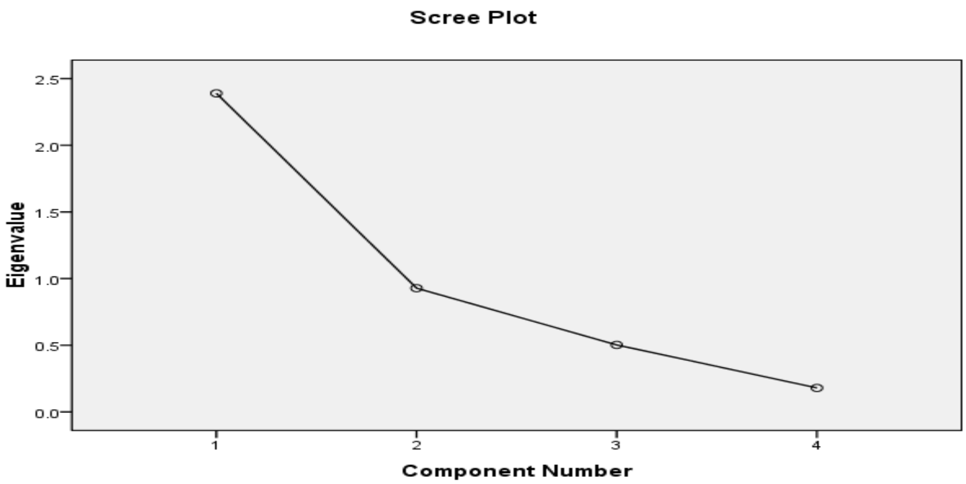

Figure 5: Showing the Scree Plot graph.

Fig 5 showsa break between components using the break point as Focus Point. Before break, it means the components are meaningful so they are retained. Therefore, the plot is meaningful at 2.390 which is the Eigen value for Cu and it drops at 2 in the component number. Also in this graph,the Eigens value which are 0.928 for Zn, 0.502 for Cd, 0.180 for lead are not meaningful.

Conclusion

The present study focused on the concentration of Zn, Pb, Cu, Cd and their pollution levels in the roadside dust along some selected locations in Ilorin town. From the study, it can be concluded that significant contamination of street dust was observed in the city of Ilorin metropolis for both season, zinc and lead were found to have the highest concentration in the dust samples and this might be as a result of the leaded gasoline combustion products in automobile exhaust emissions and industrial incinerator emissions. But it was found to be more pronounced in the first analysis which is the dry season. Significant concentrations of coppers were observed in the two seasons while cadmium was not found in the dust samples. Maybe activities in these sampled areas do not lead to the release of cadmium. Concentration of metals in soil varies in dry season and wet season due to the runoff effect that is capable of removing metals from the roadside. The statistical analysis of the measured values for the elements has indicated the level of pollution in the atmospheric environment of the street. Correlation coefficient of the metals at the ten sampling road sites for each season revealed that there is a positive relationship between all the metals during the dry season and there is a positive relationship between Cu–Zn, Cu–Pb, and Zn–Pb, while we have a negative relationship between Cu–Cd, Zn–Cd and Cd–Pb during the wet seasons. It will be recommended in this study thatcompliance monitoring should be employed on the fuel quality and vehicle emission standards. The government should come up with Regular vehicle inspection and maintenance facility in order to reduce vehicle emission rate.

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