



RESEARCH PAPER

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Evaluation of some heavy metals in roadside soil along Samaru-Giwa road, Zaria, Nigeria

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Abstract

This research work was carried out to evaluate the concentrations of some heavy metals (Pb, Cd, Cu, Zn and Mn) in roadside soil along Samaru-Giwa road, Zaria, Nigeria. Four sampling locations were selected (ABUTH, NAPRI, Marabar Guga and ABU Dam Quarters in Ahmadu Bello University, Zaria main campus which served as the control site). Soil samples were collected at 0, 50, 100 and 200 m distances from the roadside in three replicates, air dried at room temperature, sieved and kept in specimen bottles with appropriate labels pending analysis. Samples were digested and analyzed for concentrations of Lead (Pb), Cadmium (Cd), Copper (Cu), Zinc (Zn) and Manganese (Mn) using Atomic Absorption Spectrophotometer (AAS). Concentrations of these heavy metals were observed to be significantly higher at 0 m than the other distances from the roadside and this decreased with increasing distance from the roadside. There was generally no significant difference in soil heavy metal concentration at 50- 200 m from the roadside. Soil lead concentration was mostly observed to be higher than that of all other metals studied. The concentrations of heavy metals observed in the soil samples was in the order of $Pb > Mn > Zn > Cd > Cu$. The contamination factors for individual heavy metal for the locations showed low to moderate contamination by the metals. Among the locations studied, Ahmadu Bello University Teaching Hospital, (ABUTH) showed the highest concentration of the most heavy metals while ABU Dam Quarters (Control), had the lowest concentration of most of the heavy metals. The study showed that, nearness to the roadside increased the soil heavy metal concentrations and this could invariably influence the same in crops planted or farm produce being dried along the roadside.

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Introduction

Environmental contaminants are widely distributed in air, water, soils and sediments. Among the environmental pollutants, metals are of particular concern, due to their potential toxic effect and ability to bio-accumulate in ecosystems (Censi *et al.*, 2006). There has been increasing concern on the effect of vehicle emission on the environment.

Heavy metals enter the environment as a result of both natural and anthropogenic activities (He *et al.*, 2004). Heavy metals in the soil originate from many sources, which include atmospheric deposition, vehicular emission, and sewage irrigation, improper stacking of the industrial solid waste, mining activities, the use of pesticides and fertilizers (Zhang *et al.*, 2011). Heavy metals released from vehicular emission can accumulate in surface soils and their deposition over time can lead to abnormal enrichment, thus causing metal contamination of the surface soils (Fong *et al.*, 2008).

Heavy metals are important group of pollutants as they are non-biodegradable, hence are not readily detoxified and removed by metabolic activities once they are available in the environment. This may subsequently lead to their build up to toxic levels or bio-accumulation in the ecosystem. Bio-accumulation of these heavy metals in man, animals and plants result in metal poisoning (Audu and Lawal, 2005).

Some of these metals are micronutrients necessary for plant growth, such as Zn, Cu, Mn, Ni, and Co, while others have unknown biological function, such as Cd, Pb, and Hg (Gaur and Adholeya, 2004). In the last few decades, anthropogenic activities like industrial and energy production, construction, waste disposal, domestic heating system and motor vehicles are continuously contributing towards an increase in the level of heavy metals in urban soils (Lee *et al.*, 2005). Although, there have been a number of studies on heavy metals in roadside soils, majority of these have been carried out in developed countries with long history of industrialization and use of leaded gasoline.

Very few studies have been carried out in the Northern guinea savanna agro ecological zone of Nigeria. Therefore, the aim of this research was to evaluate the concentration of heavy metals in soil samples along Samaru-Giwa road, Zaria, Kaduna State, Nigeria. The result of this study will indicate the level of pollution in the studied areas and can be used by relevant authorities for environmental monitoring.

Materials and methods

Study area

The study was conducted at three locations (Ahmadu Bello University Teaching Hospital (ABUTH), National Animal Production Research Institute (NAPRI), Marabar Guga and ABU Dam Quarters in Ahmadu Bello University, (ABU), Zaria, Main campus, along Samaru-Giwa road, Zaria, Nigeria. Zaria is located at 07°33'E and 11°12'N in Kaduna State, Nigeria, within the Northern Guinea Savanna agro-ecological zone of Nigeria. Ahmadu Bello University Dam Quarters, a low traffic density area within the University, Samaru, Zaria, Nigeria, served as the control. The sampling locations were uncultivated lands characterized by different vegetation cover.

Sample Collection

Soil samples were collected using stainless steel spoon materials at a distance of 0, 50, 100 and 200 m from the roadside in three replications at 10 m apart at each distance. In each location, a total of 12 soil samples were collected. Samples collected were put in clean Polyethene bags with appropriate labels and brought to the Laboratory, Department of Biological Sciences, Ahmadu Bello University, Zaria.

The samples were spread in clean plastic trays and allowed to air dry. Plants and hard materials were removed from the samples. After seven days, soil samples were sieved using a 2 mm stainless steel sieve to remove lumps and clumps of soil together with organic materials. The sieved soil samples were kept in clean polythene bags with appropriate labels for physical and chemical analysis.

*Physico chemical properties of soil**WHO*

2011.. Lead in drinking water, Background document for Development of WHO Guidelines for Drinking Water Quality. Geneva: WHO Chronicle, **2**:31–388.

Physico - chemical properties of the soil samples, which include soil pH, Textural class and Total Organic Matter were determined at the Department of Soil Science Laboratory, Faculty of Agriculture, Ahamdu Bello University, Zaria.

Soil digestion

Soil samples were digested at the Multi-User Science Research Laboratory, Chemistry Department, Ahmadu Bello University, Zaria. Samples were digested for heavy metal analysis using the method of Ogunfowokan *et al.* (2009). In this method, each soil sample was digested with Nitric and Hydrochloric acids (HNO₃: HCl) in the ratio of 3:1. For each soil sample, 0.5 g was weighed and put in a 100 ml beaker with appropriate label and 7.5 ml of HNO₃ and 2.5 ml of HCl were simultaneously added to the beaker containing each soil sample.

The beakers were immediately placed on a thermostat hotplate at 150 °C. The samples were allowed to boil to colourless fluid before they were removed from the hotplate. Deionized water was added to make the volume to 50 ml mark. The contents were allowed to cool down to room temperature before the contents were filtered with a Whatman No.1 filter paper into a 50 ml volumetric flask. The supernatant were transferred into clean white sample bottles with appropriate labels. A blank determination was carried out using the procedure described above without the sample. The Pb, Cd, Cu, Zn and Mn concentrations were determined using Atomic Absorption Spectrophotometer (AAS).

Contamination factor (CF)

The level of contamination of soil by the heavy metals was expressed in terms of a contamination factor (CF) calculated as described by Reboredo (1993).

$CF = C_m \text{ Sample} / C_m \text{ background}$,

where: c_m sample is concentration of metal in the samples, c_m background is the background value of the metal.

Contamination factor of: $CF < 1$ refers to low contamination; $1 \leq CF < 3$ means moderate contamination; $3 \leq CF \leq 6$ indicates considerable contamination and $CF > 6$ indicates very high contamination.

Statistical analysis

Data generated from this study were subjected to one-way Analysis of Variance (ANOVA) using SPSS package Version 20. Significant differences in means were separated using Duncan Multiple Range Test (DMRT) at $P \leq 0.05$.

Results

The soil properties that were determined include pH, particles sizes and total organic matter (TOM). Soil pH of the samples ranged from 6.31 -6.97 which is an indication of being mildly acidic. Soil texture ranged between loam to sandy loam soil. Organic matter content was observed to be in the range of 0.48-3.34 % (Table 1).

The analysis of the combined data on distance from the roadside showed that, the concentration of Cu observed at 0 m from the road was significantly higher than that from 50 - 200 m from the road (Table 3). The analysis of the pooled data from all the locations showed that, the highest concentration of copper observed at NAPRI was similar to that at other locations (Table 4).

Generally, the data from most locations and the combined data analysis showed that, all the heavy metals had the highest concentrations at 0 m from the roadside. This was significantly higher than that of other distances for Pb, Cu and Zn, while that of Mn was comparable with that at 100 and 200 m, but that of Cd was similar to that observed at other distances from the roadside.

Table 1. Physical and chemical properties of the soil sampled in all the sampling locations on Samaru-Giwa road, Nigeria.

Location	Distance (m)	Clay (%)	Silt (%)	Sand (%)	Texture Class	pH	Organic Matter (%)
ABUTH	0	11	14	75	Sandy Loam	6.37	1.65
	50	7	36	57	Sandy Loam	6.45	1.07
	100	11	52	37	Silt Loam	6.68	0.48
	200	11	28	61	Sandy Loam	6.97	3.34
NAPRI	0	13	18	69	Sandy Loam	6.82	2.61
	50	7	24	69	Sandy Loam	6.85	1.89
	100	7	20	73	Sandy Loam	6.78	2.61
	200	9	22	69	Sandy Loam	6.74	1.79
Marabar Guga	0	7	26	67	Sandy Loam	6.4	1.55
	50	7	46	47	Loam	6.8	1.48
	100	9	46	45	Loam	6.74	1.09
	200	11	52	37	Silt Loam	6.62	1.79
ABU dam Quarters	0	9	38	53	Sandy Loam	6.35	2.06
	50	9	50	41	Loam	6.41	2.68
	100	9	50	41	Loam	6.31	2.61
	200	9	46	45	Loam	6.35	2.96

The higher concentration of heavy metals observed at 0 m from the roadside could be attributed in part to heavy metal emission from vehicle exhaust in particulate form or contamination due to wear of vehicle parts which are forced to settle under gravity closer to the edge of the road. This can invariably increase the heavy metal concentrations in plants, particularly crop plants near the roadside. Also, there can be danger of these metals accumulating in farm produce usually spread along roadsides to dry properly as the custom is here. According to Joshi *et al.* (2010) roadside soils consistently had greater heavy metals content for all metals than those further away. Heavy metal concentrations were generally similar between 50-200 m from the roadside.

Generally, soil Pb was observed to be higher than all other metals studied in all the sites, the concentrations of the heavy metals being in the order of Pb > Mn > Zn > Cd > Cu. Lead is especially prone to accumulation in surface horizons of soil because its low water solubility resulting in very low mobility. This might be from the deposition from automobile exhaust due to presence of tetraethyl lead as anti-

knock agent used as fuel additive. It also comes from vehicle emission of gaseous and particulate matter into the atmosphere which dissolves in moisture and fall during the rain. However, at Marabar Guga and ABU Dam Quarters (Control), lead concentration was observed to be the same in all the four distances from the roadside (Table 2).

Lead

The highest concentration of Pb (113.79 mg/kg) was observed at ABUTH and Marabar Guga while the lowest (44.83 mg/kg) was observed at ABU Dam Quarters. The observed Pb concentration was below the permissible level (90-300 mg/kg) given by WHO, (2011). A study by Ijeoma *et al.* (2011), on heavy metal content in high traffic area soils of Pakistan, recorded a minimum lead concentration of 10.06 mg/kg and a maximum Pb concentration of 29.71 mg/kg. Atiemo *et al.* (2011) recorded levels of Pb in road soils ranging from 33.64 mg/kg to 117.45 mg/kg. However, Jaradat and Momani (1999) recorded levels of Pb in roadside soils at different distances from the road ranging from 3.700 mg/kg to 272.200 mg/kg.

Table 2. Heavy metal concentration of roadside soils at some locations along Samaru-Giwa road, Nigeria.

Location	Distance (m)	Heavy metal Concentrations (mg/kg)				
		Pb	Cd	Cu	Zn	Mn
ABUTH	0	148.28 ^a	20.32 ^a	11.69 ^a	242.98 ^a	17.20 ^c
	50	79.31 ^c	13.59 ^b	3.53 ^b	30.47 ^b	21.83 ^c
	100	113.79 ^b	16.29 ^{ab}	6.25 ^b	16.04 ^c	51.80 ^b
	200	113.79 ^b	14.94 ^{ab}	7.61 ^{ab}	16.04 ^c	93.75 ^a
	Mean	113.79	16.29	7.27	76.38	46.15
	P value	0.000 ^{**}	0.110ns	0.025 [*]	0.000 ^{**}	0.000 ^{**}
NAPRI	0	147.61 ^a	16.29 ^a	11.69 ^a	46.51 ^a	100.60 ^a
	50	113.12 ^b	17.63 ^a	6.25 ^{ab}	16.84 ^b	70.63 ^c
	100	113.79 ^b	17.63 ^a	6.02 ^b	16.84 ^b	89.47 ^b
	200	44.83 ^c	17.63 ^a	6.25 ^{ab}	10.43 ^b	65.50 ^c
	Mean	104.84	17.3	7.55	22.66	81.55
	P value	0.000 ^{**}	0.931ns	0.102ns	0.000 ^{**}	0.000 ^{**}
Marabar Guga	0	113.79 ^a	18.98 ^a	4.61 ^a	72.17 ^a	119.44 ^a
	50	113.79 ^a	18.98 ^a	4.89 ^a	17.64 ^b	71.49 ^{bc}
	100	113.79 ^a	20.32 ^a	6.25 ^a	16.04 ^b	68.92 ^c
	200	113.79 ^a	20.32 ^a	4.89 ^a	19.25 ^b	78.34 ^b
	Mean	113.79	19.65	5.16	31.28	84.55
	P value	1.000ns	0.965ns	0.838ns	0.000 ^{**}	0.000 ^{**}
ABU Dam Quarters	0	44.83 ^a	27.05 ^a	7.61 ^a	34.48 ^a	69.78 ^b
	50	44.83 ^a	9.56 ^b	6.25 ^a	20.85 ^b	68.07 ^b
	100	44.83 ^a	10.90 ^b	6.25 ^a	24.86 ^{ab}	68.07 ^b
	200	44.83 ^a	10.90 ^b	7.61 ^a	22.45 ^b	93.75 ^a
	Mean	44.83	14.6	6.93	25.66	74.92
	P value	1.000ns	0.001 ^{**}	0.856ns	0.054ns	0.000 ^{**}

NB: Means followed by the same letter(s) within each column at each site are not significantly different (P=0.05), using DMRT. ns = not significant * = significant at P<0.05 ** = highly significant.

There has been a lot of attention paid to lead level in soils because it is well known to cause adverse health effects, and is relatively widespread as a result of its historical use in many commercial products, from gasoline to paints (Grubinger and Ross, 2011). Lead concentrations observed in all the locations was in the order: ABUTH and Marabar Guga>NAPRI >ABU Dam Quarters.

Cadmium

The analysis of the pooled data from all the locations showed that, Marabar Guga had the highest

concentration of Cadmium (21.33 mg/kg) which was only significantly higher than the lowest (19.65 mg/kg) at ABU dam quarters (Table 4). These values are higher than the limits given by European Union of < 3 mg/kg in unpolluted soil. In this study, all the locations had Cd concentration higher than the European Union limit. Also, the Cadmium concentration observed in this study is higher than that reported by Adedeji *et al.* (2013) from Ogun State, Nigeria, which ranged from 0.05 to 0.13 mg/kg and that of Okunola *et al.* (2007) in a similar study carried out within major and minor roads in Kaduna town, Nigeria.

The presence of Cd may have been due to lubricating oils, old tyres that are frequently used on rough surfaces of road which increases the wearing of tyres (Zhang *et al.*, 2012, Viard *et al.*, 2004, Jadarat and

Momani, 1999). Cadmium concentrations observed was in the order of Marabar Guga > NAPRI > ABUTH > ABU Dam Quarters.

Table 3. Heavy metal concentration in Soils in all the locations along Samaru – Giwa road, Nigeria based on distance from the roadside.

Distance (m)	Heavy metal concentration (mg/kg)				
	Pb	Cd	Cu	Zn	Mn
0	138.25 ^a	17.60 ^a	13.23 ^a	102.70 ^a	99.36 ^a
50	87.90 ^b	13.64 ^a	5.51 ^b	23.95 ^b	60.25 ^b
100	102.15 ^b	14.84 ^a	5.87 ^b	21.92 ^b	78.85 ^{ab}
200	84.91 ^b	14.91 ^a	6.62 ^b	20.21 ^b	81.17 ^{ab}
Mean	103.30	15.25	7.81	47.35	79.91
P value	0.009 ^{**}	0.457 ^{ns}	0.000 ^{**}	0.000 ^{**}	0.015 [*]

NB: Means followed by the same letter(s) within each column at each site are not significantly different (P=0.05), using DMRT. ns = not significant * = significant at P<0.05 ** = highly significant.

Copper

The analysis of the pooled data from all the locations showed that, the highest concentration of Copper (7.55 mg/kg) in the soil was observed at NAPRI, was not significantly higher than the lowest (5.16 mg/kg) observed at Marabar Guga (Table 4). This value is higher than 1.48 mg/kg reported by Awofolu (2005) in Lagos, Nigeria but lower than 18.00 mg/kg and 48.00 mg/kg reported by Kakula (2003) in Abuja, Nigeria, and Okunola *et al.* (2007) in Kaduna, Nigeria. The level of soil copper observed in this study was below the permissible level 135 mg/kg given by WHO, (2011). Soils naturally contain copper in some forms, ranging anywhere from 2-100 parts per million (ppm) and averaging at about 30 ppm (Schulte and Kelling, 1999).

Research works shows that copper promotes seed production, plays an essential role in chlorophyll formation and is essential for proper enzyme activity (Rehm and Schmitt, 2002). Akan *et al.* (2013) reported that, the reason for presence of Cu in roadside soil might be due to corrosion of metallic parts of vehicles such as engine wear, thrust bearing, brushing and bearing metals. In a similar work, Zakir *et al.* (2014) indicated that,

Copper in roadside soil was found to be due to corrosion of metallic parts of the vehicles such as engine wear and from brake lining wear. In all the locations Cu concentrations observed follows the order NAPRI > ABUTH > ABU Dam Quarters > Marabar Guga.

Zinc

The analysis of the combined data from all the locations also showed that, the lowest Zn concentration (22.66 mg/kg) observed at NAPRI was only significantly lower than the highest (76.38 mg/kg) observed at ABUTH (Table 4). This was below the permissible level of (300 mg/kg) in unpolluted soil WHO, (2011). Zinc in roadside soil has been found to be due to corrosion of the metallic parts of cars like engine wear, thrust bearing and brush wear (Divrikli *et al.*, 2003). On the other hand, Zinc (Zn) is one of the major pollutant of roadside soil (Yun *et al.*, 2000) and the most abundant heavy metal in roadside soil (Mashi *et al.*, 2004).

Being an essential element, the plants close to the roadside are not likely to be deficient of Zn. Zinc is an activator of some enzyme systems in plants.

Table 4. Concentration of heavy metals in Soils in all the locations along Samaru-Giwa road, Nigeria irrespective of distance from the roadside.

Heavy metal Concentration (mg/kg)					
Location	Pb	Cd	Cu	Zn	Mn
ABUTH	113.79 ^a	16.29 ^{ab}	7.27 ^a	76.38 ^a	46.15 ^b
NAPRI	104.84 ^a	17.30 ^{ab}	7.55 ^a	22.66 ^b	81.55 ^a
Marabar Guga	113.79 ^a	19.65 ^a	5.16 ^a	31.28 ^b	84.55 ^a
ABU Dam Quarters	44.83 ^b	14.60 ^b	6.93 ^a	25.66 ^b	74.92 ^a
Mean	94.31	16.96	6.73	39	71.79
P value	0.000**	0.000**	0.195ns	0.075ns	0.001**

NB: Means followed by the same letter(s) within each column are not significantly different (P=0.05) using DMRT. ns = not significant *= significant at P<0.05 **= highly significant at P>0.01.

Zinc concentrations observed in all the study locations followed the order ABUTH>Marabar Guga>ABU Dam Quarters>NAPRI.

Manganese

Combined analysis of the data based on the locations showed that, the highest concentration of Manganese (84.55 mg/kg) was observed at Marabar Guga, was only significantly higher than the lowest concentration (46.15 mg/kg) at ABUTH (Table 4).

These values are lower than those observed in some places within and outside Nigeria. The values were also below the permissible standard (1500 mg/kg) set by WHO, (2011). For example, Yauri 608.11 mg/kg (Yahaya *et al.*, 2009), Kaduna 132 mg/kg (Okunola *et al.*, 2007), United States, 2532 mg/kg (Abida *et al.*, 2009) and China 1740 mg/kg, (Bradford *et al.*, 1996).

Table 5. Contamination factor of soils heavy metals at different locations along Samaru-Giwa road, Nigeria.

Location	Contamination factor				
	Pb	Cd	Cu	Zn	Mn
ABUTH	2.54	1.12	1.05	2.98	0.62
NAPRI	2.34	1.18	1.09	0.88	1.09
MARABAR GUGA	2.54	1.35	0.74	1.22	1.13
ABU DAM QUARTERS	1.00	1.00	1.00	1.00	1.00
Mean	2.11	1.16	0.97	1.52	0.96

Contamination factor calculated for the heavy metals in the various locations ranged from 0.74 to 2.98. The highest contamination factor of 2.98 for Zn at ABUTH indicates moderate contamination; therefore all the studied locations had low to moderate contamination by these heavy metals (Table 5).

Manganese is a naturally occurring mineral found in many types of rock and soil; it is ubiquitous in the environment and found in low levels in water air, soil, and food (ATSDR, 1997).

Manganese is involved in activation of enzyme systems and chlorophyll synthesis in plants. Sources of manganese due to human activities in the environment include; combustion of coal, fuel,

residential combustion of wood, iron and steel production plants and power plants (Calkins, 2009). Manganese concentration of all the study locations followed the order: Marabar Guga>NAPRI >ABU Dam Quarters>ABUTH.

Conclusion

In conclusion, heavy metal concentrations were observed to decrease with increasing distance from

the roadside, being highest between 0-50 m. There was generally no significant difference in soil heavy metal concentration at 50 -200 m from the roadside in most of the locations studied. Among the studied locations, ABUTH and Marabar Guga showed high concentrations of most of the heavy metals studied particularly Pb, Zn and Mn, while ABU Dam Quarters (the control) showed the lowest concentration of most of the heavy metals. The study showed that, nearness to the roadside increased the soil heavy metal concentration and this could invariably influence the same in crops planted near roadside or harvested crops being dried by the roadside as the custom is here.

Contamination factor calculated for the heavy metals in the various locations ranged from 0.74 to 2.98. The highest contamination factor of 2.98 for Zn at ABUTH indicates moderate contamination; therefore all the studied locations had low to moderate contamination by these heavy metals (Table 5)

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