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DISTRIBUTION OF SOME BIOGENIC HEAVY METALS IN ROADSIDE SOIL FROM SELECTED HIGHWAYS IN URBAN KANO CITY, NIGERIA

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Abstract: *This study determined and evaluated soil properties and distribution of some biogenic (copper, iron, manganese and zinc) heavy metals in the road side soil at six sites in urban Kano city. Six composite samples 20m apart were taken from the roadside soil. Particle size distribution was determined by the used of hydrometer method as modified by Bouycous. Soil pH was determined in distilled water (1:1 water: soil) using the glass electrode pH meter. Organic carbon was determined by potassium dichromate wet oxidation method of walkley and black. Total nitrogen was determined by the micro-kjeldhal digestion method. Exchangeable acidity was determined by leaching soil samples with neutral molar solution of KCl and the acidity estimated by titrating with 0.02M NaOH solution using phenolphaliene as indicator. Exchangeable bases (Ca, Mg, K and Na) of the soils were extracted using 1N neutral ammonium acetate (NH_4OAC) and (Cu, Zn, Fe, Mn) ware determined using Microwave Plasma Atomic Emission Spectroscopy (MPAES machine). The biogenic trace metals were evenly distributed in the Roadside soil. The results of biogenic metals were lower than the limits set by the Swedish Environmental Code, NASREA, SON and WHO. Surprisingly the soils were enriched. Some of the metal contents could in the long term enhance health and environmental concerns, especially at school and children's day centers located close to the roadsides of KTN, KRW and KNL where the risk of repeated exposure was apparent. More investigations are justified to verify these risks.*

Keywords: *biogenic, heavy metal, soil, highways.*

INTRODUCTION

The terms "Bio" means life or associated with life, the term biogenic means essential for maintaining the fundamental life processes , Biogenic heavy metals means the metals essential for maintaining the fundamental life processes ,those metals are Cu, Fe, Zn, Mn, Mo and Se (Murry, 2002) Cr and Cd sometimes play an important role in life processes, all matters in the universe occurs in the form of small numbers of elements, there are 92 naturally occurring chemical elements in the universe, almost every one of the chemical plays some role in the earth living systems. However the 20 elements account for the vast majority in the living system (Murry, 2002).

The biogenic elements are divided into six major elements (element found in almost all of the earth's living system in relatively large quantity). Carbon (C),Hydrogen (H), oxygen (O),Nitrogen (N),Phosphorous (P) and Sulphur (S).Five minor biogenic elements (elements found in many earth living systems in relatively small quantities), Sodium (Na), Potassium (K), Magnesium (Mg), Calcium (Ca) and Chlorine (Cl). Trace elements (Essential elements necessary only in very small quantities to maintain the chemical reaction on which life defense found only a very few on the earth living systems), Iron (Fe), Cobalt (Co), Zinc (Zn), Boron (Br), Aluminum (Al), Vanadium

(Vn), Molybdenum (Mo), Iodine(I), Silicon (Si), Nickel (Ni) and Bromine (Br), (Murry, 2002). Heavy metals are metals with a density at least five times that of water , heavy metals is the term commonly adopted as a group name for the metals which are associated with pollution and toxicity , they may also include some elements which are very essential for living organism at low concentration , Among these heavy metals some have been found to be serious hazard to plants and animals and have listed by the European commission to include As, Cd, Cr, Cu, Pb, Hg, Ni, Al and Zn (Dolan *et al*., 2006)). Heavy metals have the ability to enter the human body through inhalation, ingestion and dermal contact absorption. They also accumulate in soils, plants and in aquatic biota (Obodai *et al.,* 2011; Suciu *et al.,* 2008; Wuana and Okieimen, 2011). Heavy metals can persist for a long time within different organic and inorganic colloids before becoming available to living organisms. They are non-degradable and therefore do not decay with time. Heavy metals can be biomagnified if an organism excretes it slower than it takes in. They can therefore become dangerous to human beings and wildlife (Adelekan and Abegunde, 2011; Kumar *et al.,* 2010). They also have relatively high densities (Obodai *et al.,* 2011).

STUDY AREA

Kano is the state capital of Kano state in North West, Nigeria. It is situated in the Sahelian geographic region, South of the Sahara, It is located between latitude 11°59’59.57’′N to 12°02’39.57’’N and longitude 8°31’19.69’’E to 8°33’19.69’’E, with a total urban land area of 137Km^{2}and 499Km^2 metropolitan area (Figure 3.1). It is made up of six Local Government Areas (Dala, Fage, Gwale, Municipal, Nasarawa,
and Tarauni) and some parts of Kumbotso, Ungogo, and Tofa Local Government Areas. Kano metropolis has an estimated population of over 4 million people with a male – female ratio of about 1 to 1.32 (Ibrahim, 2014). Over 70% of the adult workforces draw their livelihoods off agriculture. Kano is the biggest commercial and industrial centre in Northern Nigeria. It has 43 existing marketplaces and over 400 privately owned manufacturing industries (Ibrahim, 2014). Kano metropolis is about 481 meters (or about 1580 feet) above sea level. The climate is a hot, semi-arid type with an annual average rainfall of about 690 mm (27.2); majority of which falls from June through September. The temperature is generally very hot throughout the year, though from December through February, the city is relatively cool. The average nighttime temperatures in the cold months range from 11° to 14°C. The vegetation therefore, is a savanna type.

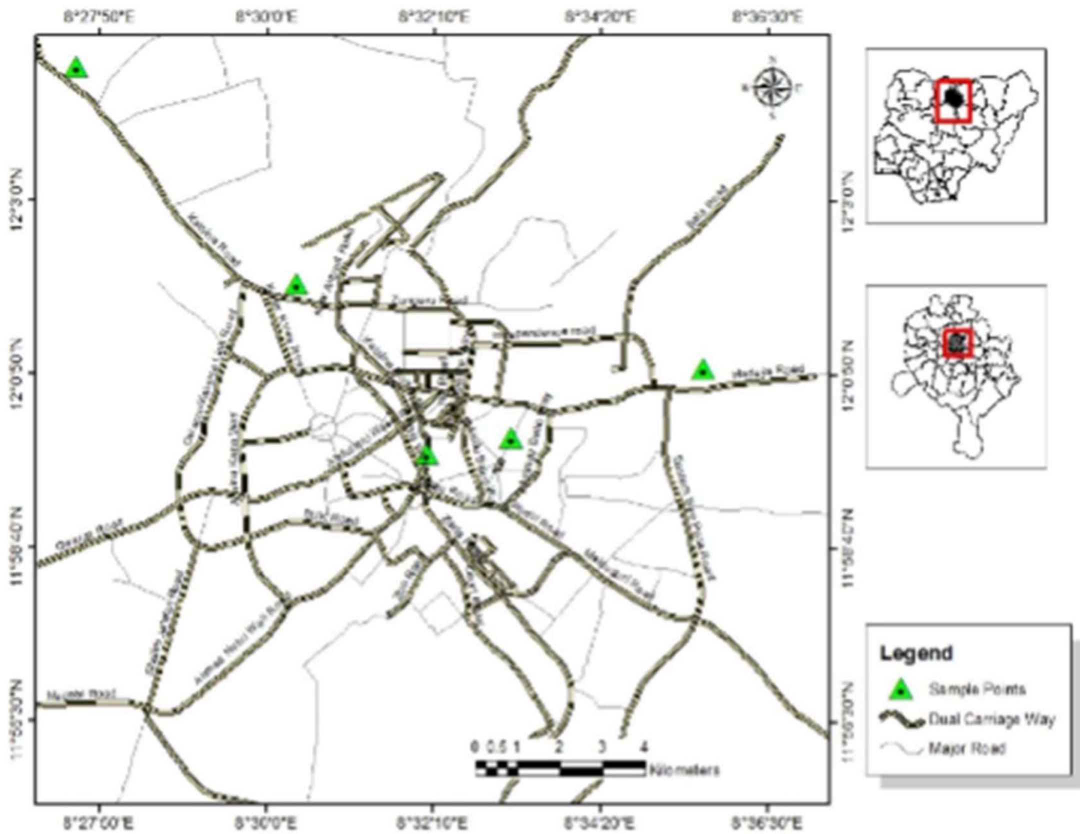

Figure. 1 Kano Metropolis Showing tthe Selected Roads for the Study.

MATERIALS AND METHODS

All reagents used were of analytical grade purity. A clean laboratory and a fume cupboard were used for preparing the samples. Deionized water was used throughout. All solution were stored in high density polyethylene bottles. All glass wares were cleaned by soaking in 10%(v/v)HNO_3

For 24hrs rinsing three times with Deionized water and dried in an oven before used. All operations were performed on a clean laboratory bench.

Sampling and Sample Pre-treatment

The soil samples were collected at different locations along the busy roads of Naibawa Zaria Road (NYL), Hadeja Road (HDJ), Kano Line Road (KNL), Kofar Ruwa Road (KRW), Katsina Road (KTN) And Nasarawa Sultan Road (GRA), within Kano city, Nigeria. Each road was divided into six segments, at each segment several soil samples were collected at random and at either side of the roads to make a one composite soil sample representing that segment (Qasem *et al*, 1999), all the samples were collected at the depth of 15cm and 5m away from the road using stainless steel auger (Olukanni, *et al*., 2012). The samples collected were placed in a clean plastic polyethene bags to minimize sample contamination and labeled immediately at the point of collection for proper identification (Baba *et al*, 2009). The collected soil sample was transported to laboratory for analysis, the hand driven auger were washed with detergent and rinsed with deionized water after each sampling(Awofolu, 2005).

Preparation of Soil Samples

The entire six soil samples collected were air dried and ground using ceremic pestle and mortar to ensure homogeneity. The soil samples were sieved through 2mm sieve and then placed in a clean plastic bags and sealed pending digestion and analysis.

Sample Digestion

Nitric-perchloric acid digestion was performed following the procedure recommended by the AOAC (1990). One gram of the soil sample was placed in a 250cm³ digestion tube and 10cm³ of con.HNO_3 was added. The mixture was boiled gently for 30-45min to oxidize all easily oxidizable . After cooling, 5cm³ of 70% $HClO_4$ was added and the mixture was boiled gently until white denmatterse fumes appeared, after cooling, 2cm³ of deionized water was added and the mixture was boiled further to release any fumes. The solution was cooled further filtered through whatman NO. 42 filter paper and transferred quantitatively to a 25cm³ volumetric flask and made up to the mark with deionized water. Triplicate samples were carried out with same procedure.

Particle Size Determination

Particle size distribution was determined by the used of hydrometer method (Bouycous, 1951) as modified by Bouyoucos day (1965).

Soil pH was determined in distilled water (1:1 water: soil) using the glass electrode pH meter.

Soil Organic Carbon

Organic carbon was determined by potassium dichromate wet oxidation method of walkley and black (1934).

DETERMINATION OF CATION EXCHANGE CAPACITY

5g of the soil was accurately weighed, and transferred to 50cm^3 centrifuge tube. 25cm^3 of 1.0M NaOAc solution was added to the tube, covered with stopper and shaken in a mechanical shaker for 5minutes. It was then centrifuge at 2000rpm for 5minutes for the supernatant to be cleared. The liquid was decanted completely and the extraction procedure was repeated three more times. Instead of NaOAc, CH_3CH_2OH was used to bring the electrical conductivity to less than 40mS/cm. to displace the sodium adsorbent, 1.0M NH_4OAc was used. After shaking and centrifuge three times with NH_4OAc, the supernatant was collected through filtration in 100cm^3 volumetric flask and made up the volume with NH_4OAc solution. The sodium concentration was determined by flame photometer (Jenway model PFP 7flame photometer) after a series of known concentration in the range of 1-10ppm of sodium calibration (Estefan *et al*., 2013)

Sample Analysis

Standard solutions were run to obtain their standard calibration curves for the examination of Zn, Mn, Fe and Cu metals under investigation. The curves showed excellent linearity across the concentration range. The large linear dynamic range means that less sample solution are needed which unproven productivity and reduced the risk of the sample contamination.

The heavy metals were analyzed from solution of the metals by Microwave- atomic emission spectrophotometer (MP-AES) at the National Metallurgical Development Center, Jos (NMDC) Research laboratory for all the elements in a single measurement. The ability of the MP-AES to determine all the elements in a single measurement has greatly simplified the work when compared to flame atomic absorption spectroscopy.

Statistical analysis

One-way analysis of variance (ANOVA) and least significant difference test were performed to evaluate statistical significance. Statistical significance was considered at $p<0.05$.

Results

The results of the physiochemical parameters and mean concentrations of some biogenic and non-biogenic heavy metals (Fe, Mn, Zn, Cu, Pb, Cd, As and Cr) in roadside soil from the six major roads in urban Kano state, (Nasarawa State road (G R A), Kofar Ruwa road (KRW), Naibawa Zaria road (NYL), Hadeja road (HDJ), Kano line road (KNL) and Katsina road (KTN) are presented in table 1 and Figure 2-6.

Table 1 Physicochemical parameters of the soil samples analyzed

Sample	pH	% Sand	% Clay	% Silt	%O.M	CEC(cmol+kg)
GRA	6.5±0.01	63.00±0.92	13.30±0.76	23.70±0.40	1.14±0.01	1.80±0.15
KNL	5.8±0.06	60.45±0.43	23.02±0.33	16.53±0.19	2.02±0.05	3.03±0.01
KTN	6.3±0.06	64.55±0.5 0	22.70±0.13	12.75±0.21	1.76 ±0.01	3.02±0.01
KRW	6.0±0.06	62.90±0.34	24.05±0.23	13.05 ±0.08	1.68 ±0.01	2.46±0.05
NYL	6.4±0.05	65.00±0.58	22.11±0.23	12.89 ±0.13	1.60±0.01	2.75±0.08
HDJ	5.7±0.01	70.50±0.36	17.91±0.06	11.59 ±0.01	1.00±0.01	1.98±0.04

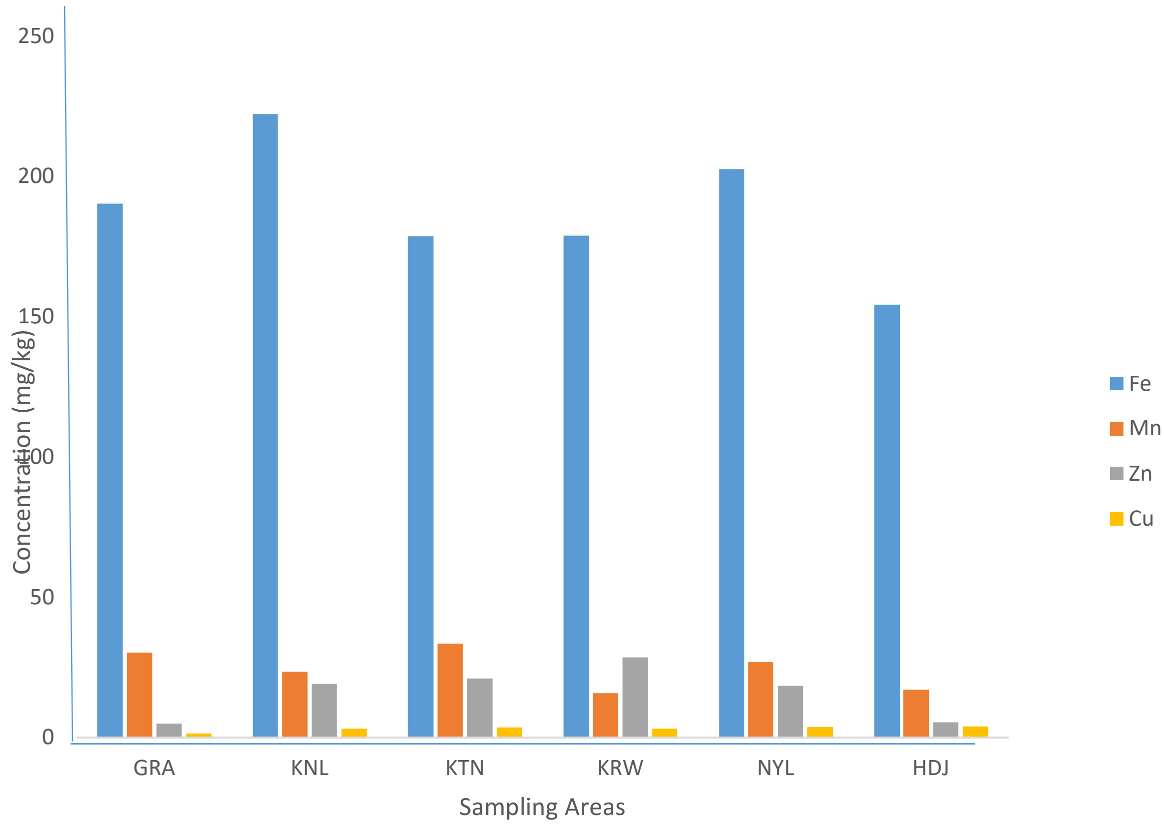

Figure 2 Mean concentrations of biogenic heavy metals in roadside soil samples from selected highways in urban Kano city.(mg/kg)

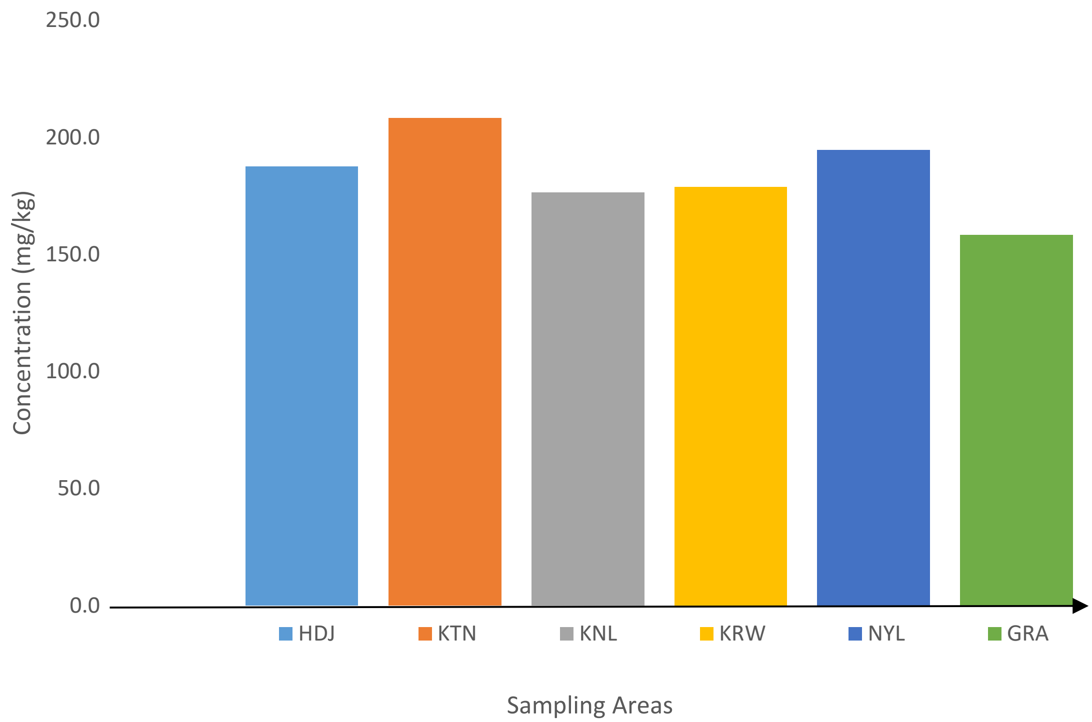

Figure 3 Concentration of Iron (Fe) in the soil samples from the sampling areas (mg/kg)

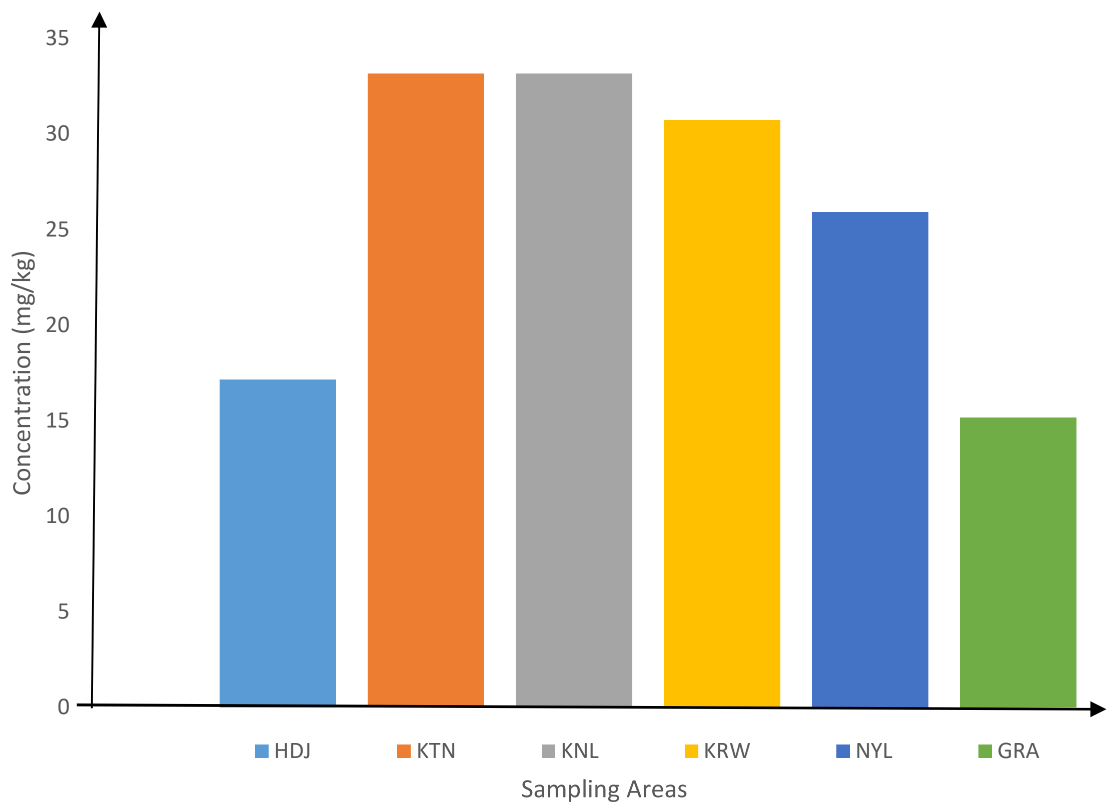

Figure 4 Concentration of Manganese (Mn) in the soil samples from the sampling areas (mg/kg)

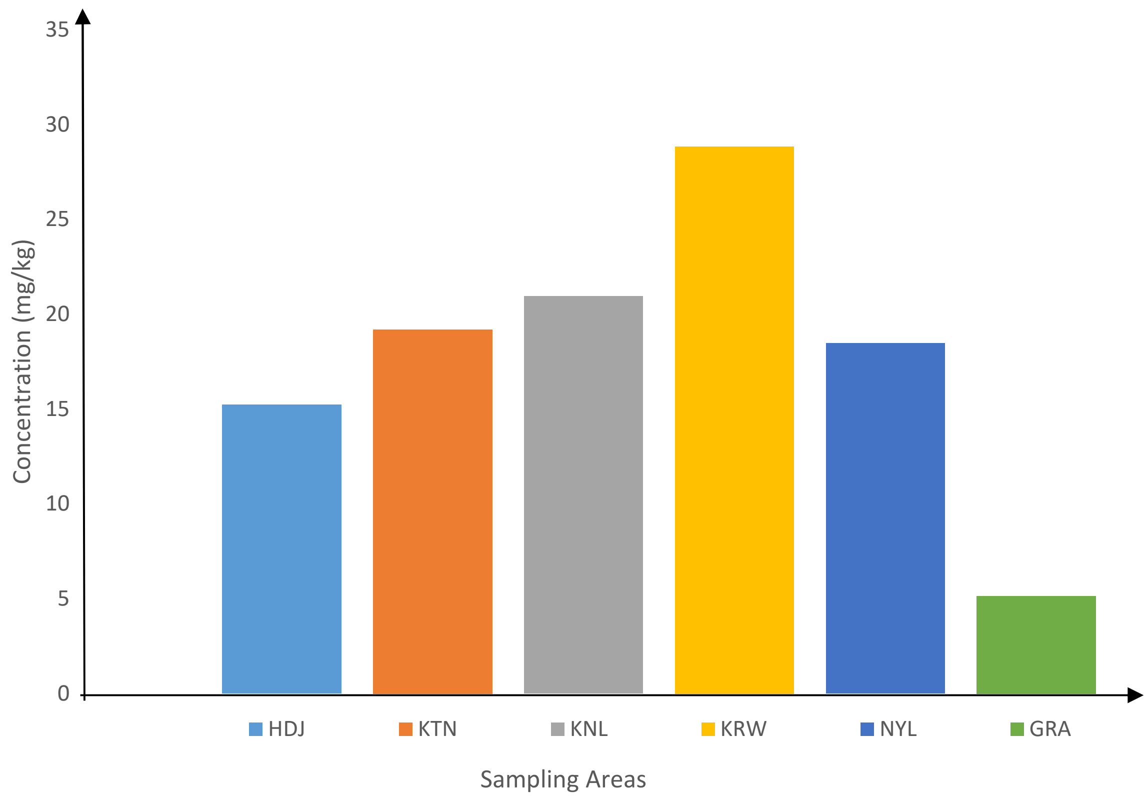

Figure 5 Concentration of Zinc (Zn) in the soil samples from the sampling areas (mg/kg)

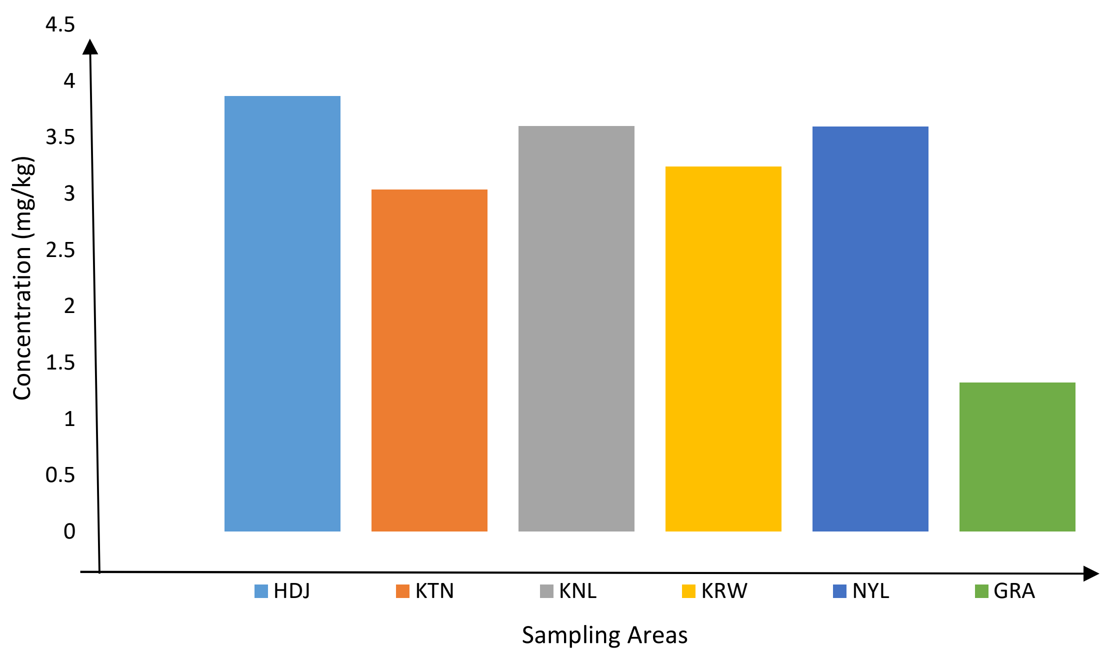

Figure 6 Concentration of Copper (Cu) in the soil samples from the sampling areas (mg/kg)

Discussion

The physiochemical characteristics of soil such as pH, organic matter, cation exchange capacity and particle size distribution are known to influence the interaction and dynamic of metals within the soil matrix. The results of the physiochemical characteristics of the soils are summarized in table 1 above.

The mean pH values of the roadside soil samples in the study areas ranged from 6.0 to 6.9 as shown in table 1 above, this indicated that the soil sample with pH less than 7 are slightly acidic, while those with pH above 7 are slightly alkaline in nature. All the soil from the roadside samples have pH values slightly above the FAO (2008), WHO (2007), NASREA (2021) and NAFDAC (2022), standard of 7. The soil pH is a major factor influencing metal chemistry, therefore the movement of these cations from the surface to the under laying soil layer will be definite. These values are inline similar with Banjako and Sobulo (1994). ANOVA results showed there was significant difference among the separate mean pH obtained from the six sampling location (P=<0.05).

Soil organic matter (SOM) enhances the usefulness of soil for agricultural purpose. It supplies essential nutrients and has capacity to hold water and absorb cations. It also functions as a source of food for soil microbes and enhance control their activities (Brady, 1996). The organic matter in soil obtained from the roadside soils varied from 1.00% to 2.02% which is below the FAO (2008), NASREA (2021) and WHO (2007,) permissible limits. Ayolagha and Onwugbuta (2001) also demonstrated that high SOM(>2.00%) in soils is conductive for heavy metal chelation. Organic matter is a reservoir of essential and non-essential mineral elements for plant growth and development, hence increased soil productivity (Anikwe and Nwobodo, 2001). The soil organic matter in the soil obtained from this study is similar with the values of 1.03 to 3.14% reported by Amos *et al*., (2014) for assessment of some heavy metals and physiochemical properties in surface soil of municipal open waste dumpsite roadside soil Yenagoa, Nigeria. ANOVA results for SOM obtained from the six locations showed that the separate SOM values were significant differences (P=<0.05). The cation exchange capacity is the amount of exchangeable cation per unit weight of dry soil that plays an important role in soil fertility. It defends o the pH, clay and on the soil organic matter content. The results of this study reveal that soil from the roadside soil had lower values of cation exchange capacity ranges from 1.80 to 3.02cmol(+)/kg. It can regulate the mobility of metals in soil and increase as pH increases (Brummer and Hermes, 1998). The CEC in the soil obtained from this study is lower than the values of some heavy metals and physiochemical properties in the surface soil of municipal open waste dumpsite roadside in Yengoa, Nigeria. ANOVA results for CEC obtained from the six locations showed that the separate CEC values were significant differences (P=<0.05).

Levels of Some Biogenic Heavy Metals in Roadside Soil Samples

Figure 2 summarized the mean concentration of some biogenic heavy metals across selected roads in urban Kano city. This figure clearly indicates that Fe (201mg/kg) and Mn (33.34mg/kg) have the highest mean concentrations, while Zn (29.0mg/kg) and Cu (3.90mg/kg) have the lowest concentrations in all the selected roadside soil samples. Figure 3 to Figure 6 indicates mean concentration of each metal at each selected roadside.

Iron (Fe)

KTN (221.93mg/kg) and NYL (202.61mg/kg) have the highest mean concentrations of Fe in the roadside soil samples, followed by HDJ (190.25mg/kg), KRW (178.49), KNL (178.57) and GRA (154.19) with the lowest mean concentration in the samples (figure 3). Iron was found to be a dominant metal when compared with other heavy metals, is vital for almost all living organism in variety of metabolism process, including oxygen and electron transport as well as DNA synthesis. Fe is very important for decreasing the incidence of anemia; the results of Fe in this study appeared to be the highest metal among all the heavy metals determined, with a range of 153.19mg/kg to 222.16mg/kg, comparing the result of iron with mean concentration of 634mg/kg to 654.99mg/kg reported by Eneje and Lemoha, (2012). W.H.O (2007), NASREA (2009), NAFDAC (2010) etc Maximum allowable limit for iron in roadsides soil sample which is 50,000mg/kg. All the samples studied are below the limits. The result showed that there was significant difference among the iron obtained from the sampling areas (p=<0.05). The mean concentration of **Mn** in the roadside soil samples ranges between 15.21mg/kg to 33.34mg/kg (figure 4) which is below the permissible limit by FAO/WHO (2007) (200/300mg/kg) (Devi *et al*., 2014). The higher concentration of Mn at the roadside soil was found to be at KTN (33.34mg/kg), KNL (33.21mg/kg) and KRW (30.73mg/kg), the lowest Mn concentration was found at GRA (15.21mg/kg), Mn is one of the most abundant element in the earth crust. The deficiency of manganese in the human body can produce severe skeletal and reproductive abnormalities and high dose of manganese produced adverse effect in the lungs and the brain (Hardey *et al.,* 2013), the level of Mn in the soil samples of this study were far below the limit. Johann *et al*., (2009) reported Mn content in the range of 15.02mg/kg - 17.10mg/kg and 35.05mg/kg –40.14mg/kg with the mean concentration of 16mg/kg and 27mg/kg in the roadside soil of Yahaya Gusau road, Katsina state, also Devi *et al*., (2010) recorded 38.50mg/kg as mean concentration of Mn in various roadside soil samples of Dutsinma road, there values are almost similar to those reported in this study. ANOVA results also showed there was significant difference at the level of Mn accumulated from the sampling areas at (p=<0.05).

Zinc (Zn), KRW (28.85mg/kg), KNL (20.95mg/kg), KTN (19.20mg/kg) and NYL (18.47mg/kg) roads have the highest mean concentration levels of zinc in roadside soil sample followed by HDJ and GRA (15.23mg/kg) and (4.90mg/kg) respectively with lowest concentrations (figure 5). According to the W.H.O (2007) the maximum allowable limit of zinc in roadside soil sample is 200mg/kg and EU (2010) 300mg/kg (Devi, *et al,* 2014). The concentrations of Zn in this study are lower than the concentration values of 232.30mg/kg to 300mg/kg reported by Chukwulobe and saeed, (2014). All the samples in this study are within the normal range. Leung, *et al.,* (2006) reported the Zn concentration recorded for this study were lower because of the differences in the sampling areas and the method used on the determination of metals in the roadside soil samples. High level of zinc can also influence the activity of microorganisms and earthworms there by retarding the breakdown of organic matter (Wuana and Okieimen, 2011). ANOVA result showed there was significant difference between the Zn obtained from the sampling areas (p=<0.05).

The mean range concentration of **Cu** in the roadside soil samples was 1.32mg/kg to 3.86mg/kg. The highest concentration of Cu in the soil samples analyzed was observed at HDJ (3.86mg/kg), KNL (3.60mg/kg), NYL (3.58mg/kg) and KTN (3.03mg/kg) this might be due to availability of metal scrap around the area while the least value was at GRA (1.32mg/kg) (figure 6). It is known that Cu is an essential element, it may be toxic to both humans and animals, when its concentration exceed the safe limits and its concentration in some human tissue like thyroid can change, depending on the tissue state. The range of Cu concentration in this study is 1.33mg/kg to 3.90mg/kg, though the concentration of Cu in all the sample site were lower than the maximum permissible limits for Cu by EU (2007), (140mg/kg), NASREA (2009), (100mg/kg), etc. the most probable source of Cu in the roadside soil is corrosion of metallic parts, wear and tear of cars engines, and spillage of lubricants (Adelaken and Abegunde, 2011). The concentration of Cu in soils obtained in this study is similar to the concentration values of 1.0 to 4.90 mg/kg reported by Shemang, (2016) for his work on the determination of some heavy metals in roadside soil samples in highways road of Kafanchan metropolis, Kaduna, Nigeria. ANOVA results showed that there was significant difference among the Cu obtained from the sampling areas (p=<0.05).

Geoaccumulation index (I_{geo})

The degree of pollution of the highways roadside soil by the metals was assessed using the Geoaccumulation index (I_{geo}) classification (table 2) by Forstner *et al*., (1993). Based on the classification the highways soil from all the sampling areas (GRA, KTN, KNL, KRW, NYL and HDJ) were found to be moderate contaminated with Zn and Mn. for that of Zn (I_{geo}=0.42 to 2.98) shows that KRW, KNL, KTN, NYL and HDJ was found to be moderate contaminated.

Table 2 Geoaccumulation index (I_{geo}) of heavy metals in the highways roadside soil

Location	Fe	Zn	Mn	Cu
GRA	0.01	0.42	0.92	0.78
KTN	0.02	2.31	1.54	0.69
KNL	0.34	2.44	1.55	0.86
KRW	0.31	2.98	1.43	0.70
NYL	0.14	2.26	1.08	0.18
HDJ	0.24	2.33	1.04	1.04

Table 3 Geoaccumulation index classification

I_{geo}	I_{geo} Class	Contamination intensity
>5	6	Very strong
>4-5	5	Strong to very strong
>3-4	4	Strong
>2-3	3	Moderate to strong
>1-2	2	Moderate
>0-1	1	Uncontaminated to moderate
<0	0	Practically uncontaminated

CONCLUSION

This study shows the presence of some biogenic and non-biogenic heavy metals (Fe, Zn, Cu and Mn) in the roadside soil samples of the selected major roads in urban Kano State. The metals are mostly originated from many sources like filling stations, battery waste, spillage of engine car oil, local industries along the roadside such as welding, vulcanization mechanics, iron bending and electrician discharging metals scrap into the environments. The Biogenic heavy metals determined the soil contained considerable amount of Fe, Mn, Zn and Cu, evenly distributed in the soils None of the samples site exceeds the maximum permissible limits; this indicates there is definite contamination in the sampling sites.

Heavy metals mean concentrations in roadside soil samples were higher than those in the control side. Though the levels of contaminants ware within the maximum permissible limits set by some international organizations like WHO, EU, FAO, NASREA, SON, NAFDAC etc, the high concentration of these metals in the roadside soil samples may be attributed to metals construction work, iron bending and welding of metals, at the same time, the traffic situation in KTN, KRW and KNL might be regarded as a source of all heavy metals content in the roadside soil. The distribution of heavy metals among the highways roadside soil and their interaction effect in the sites were interpreted using ANOVA. The result of ANOVA indicated that there was significant differences in the levels of most metals between the six sampling areas.

RECOMMENDATIONS

It is recommended that further research should be carried out into the following;

1. Health risk assessment should be carried out periodically on the people and inhabitants closed to the road to check for some symptoms of heavy metals inhalation.

2. Concentrations of other heavy metals in the roadside soil samples of the sampling areas should be constantly monitored.
3. There should be routine monitoring of heavy metals contents of the samples of the areas to ensure safety to both humans and animals in particular and the environment in general.
4. It is also recommended that regular monitoring of levels of heavy metals in major roads of Kano state metropolis is encourage to ensure suitable management of the urban environment and reduction of traffic related contamination of roadside soils.

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