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

[1]Habibu, F.H. and [2]Mohammed, M.I.
Department of Pure and Industrial Chemistry, Bayero University, Kano, Nigeria

Abstract: *Heavy metal concentration in road side soils with its potential ecological effects draws much attention in the developing countries. This necessitates the study of their accumulation in the road side soils of Kano (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 to ensure effective protection of soil from the potential loss of its fertility. In this study, roadside soil samples from six major roads (Kano line, Katsina road, Kofar ruwa road, Hadeja road, Zaria road and Nassarawa GRA road) were collected and determined the levels of heavy metals (As, Cr, Pb, and Cd,) in the roadside soil ware determined using Microwave Plasma Atomic Emission Spectroscopy (MPAES machine), 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). The distribution of non-biogenic metals may suggest anthropogenic source of the metals. Metal accumulation, especially Pb, Cd, and Ni did not conform to trends of traffic intensity. 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.*

Keywords: *Non-biogenic, heavy metals, pollution, soil.*

INTRODUCTION

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, 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). Theses heavy metals are released into the roadside environment as a result of mechanical abrasion and normal wear and tear. Soil tends to accumulate metals on a relatively long term basis since many metals in the soil are mobile. The heavy metals present in soils can be transported to plant or animals by the action of water or wind. This may affect the quality of water and air. Inhalation, ingestion or dermal contact may post a severe risk to ecosystem and threaten human health. Heavy metal concentration in soil with its potential ecological effects has been a worldwide environmental concern for long time and attains much attention in the recent past. Therefore, it is necessary to have a continuous study on the accumulation of heavy metals in the soil to ensure effective protection of soil from the potential loss of its fertility**.**

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).

The Non-Biogenic metals are Lead (Pb), Cadmium (Cd), Chromium (Cr), Arsenic (Ar), Nickel (Ni) and Wolfram (Wo). The role of heavy metals in the soil is increasingly becoming an issue of global concern at private and governmental levels, especially as soil constitutes a crucial component of rural and urban environment and can be considered as a very important (USDA 2001).

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.

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.

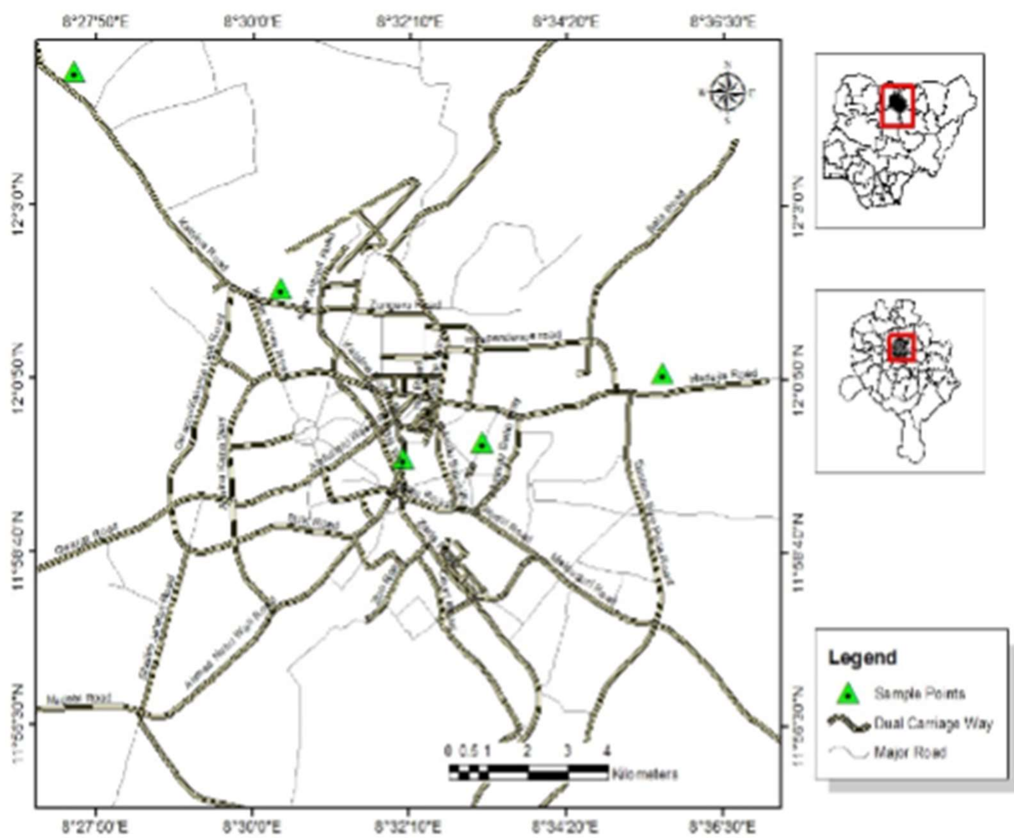

Figure 3.1 Kano metropolis showing the selected roads for the study.

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 50cm³ centrifuge tube. 25cm³ 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 As, Cr, Cd and Pb, 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 non-biogenic heavy metals (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 4.1 and Figure 4.1 – 4.10.

Table 4.1 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

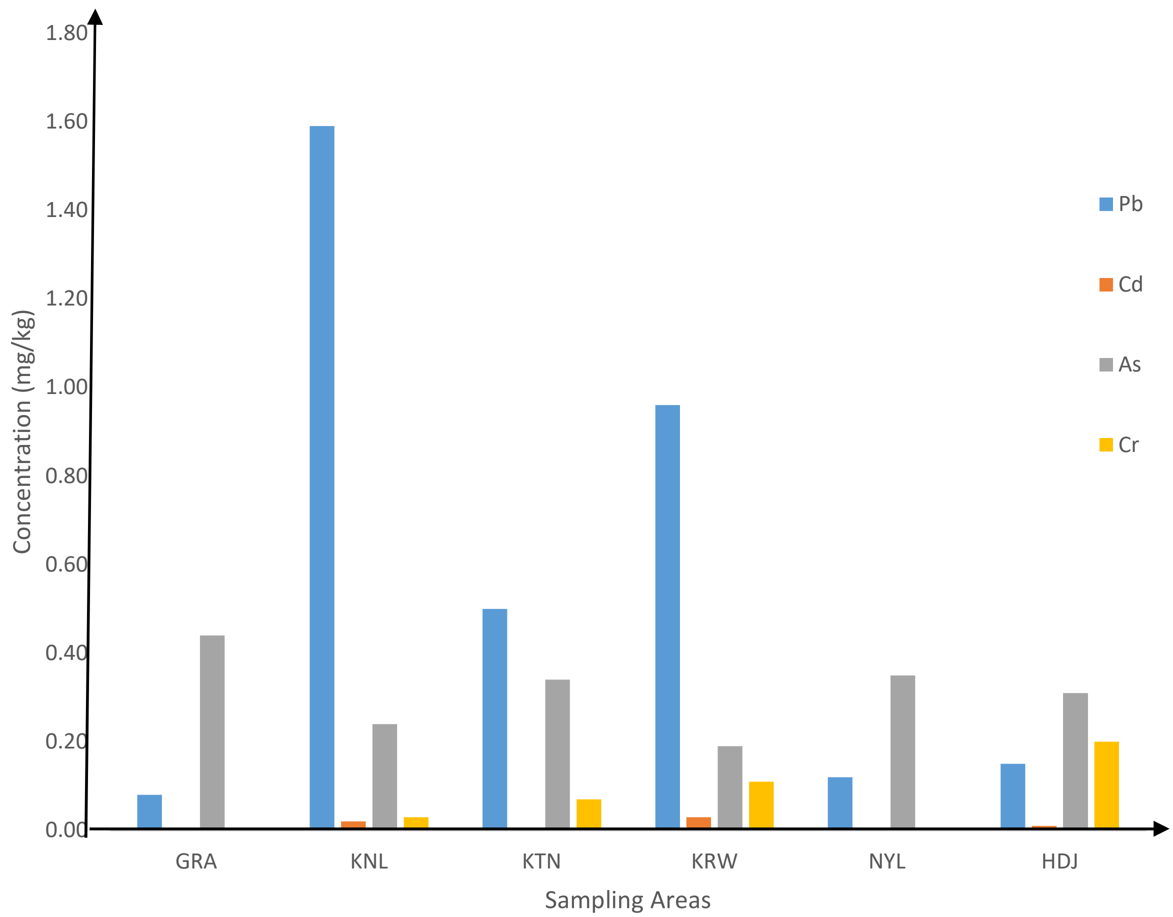

Figure 4.6 Mean concentrations of non-biogenic heavy metals in roadside soil samples from selected highways in urban Kano city. (mg/kg)

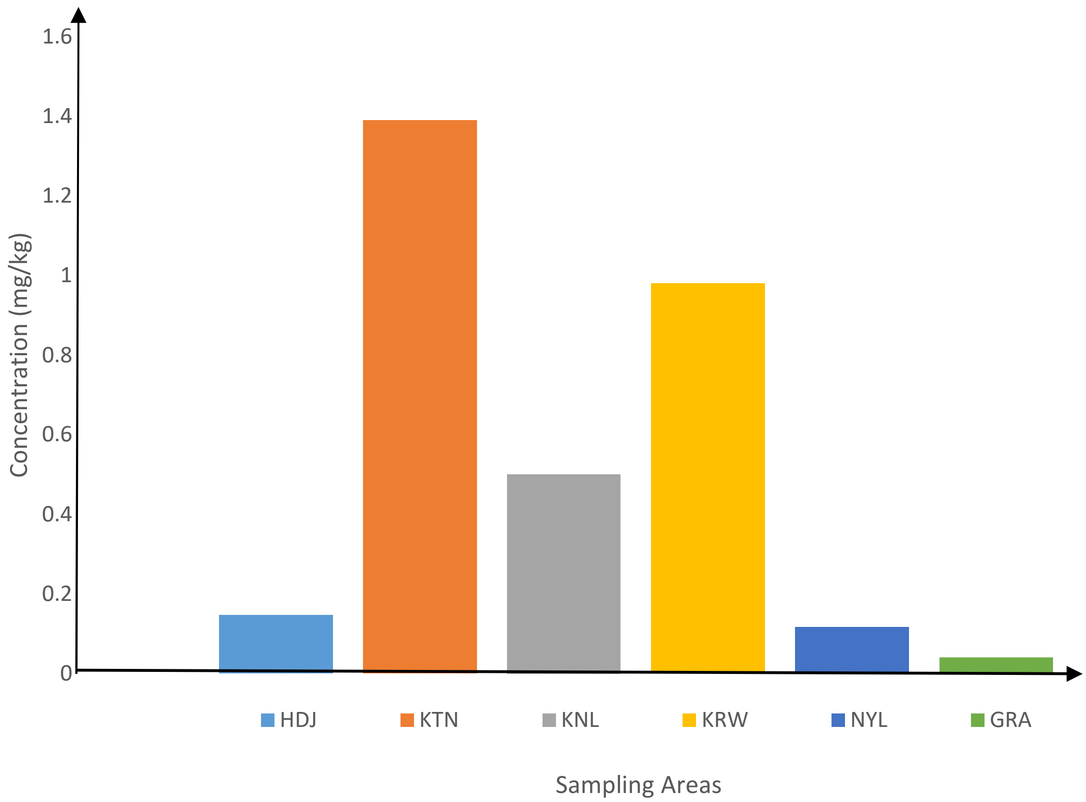

Figure 4.7 Concentration of Lead (Pb) in the soil samples from the sampling areas (mg/kg)

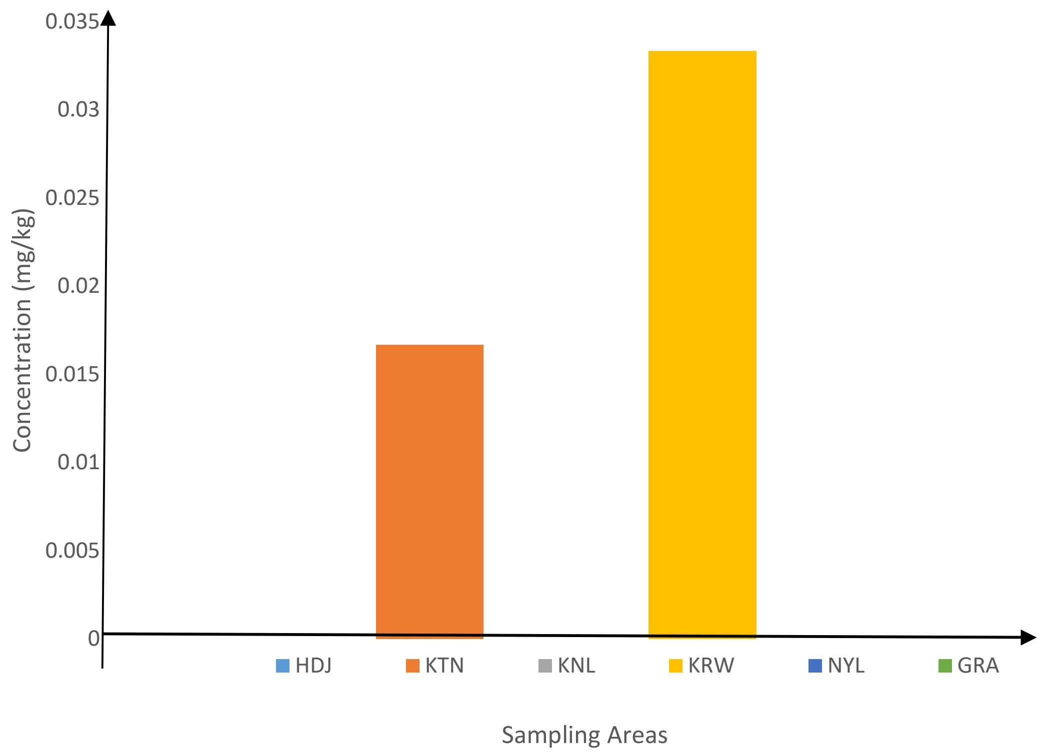

Figure 4.8 Concentration of Cadmium (Cd) in the soil samples from the sampling areas (mg/kg)

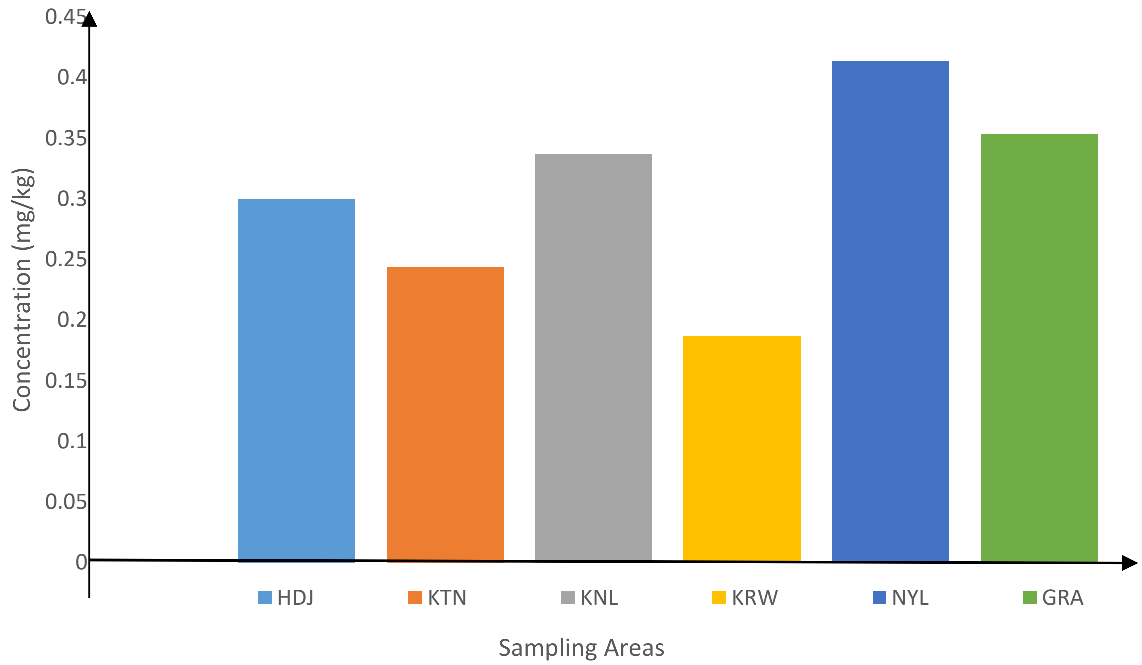

Figure 4.9 Concentration of Arsenic (As) in the soil samples from the sampling areas (mg/kg)

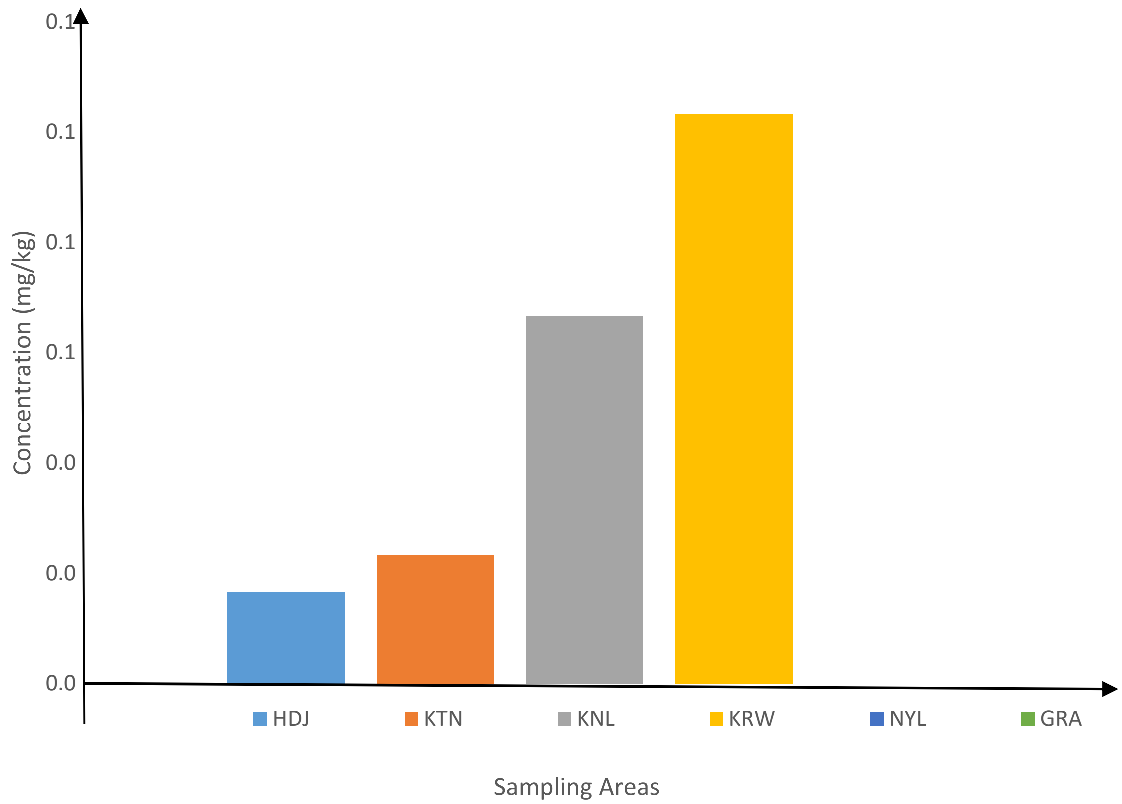

Figure 4.10 Concentration of Chromium (Cr) in the soil samples from the sampling areas (mg/kg).

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 4.1 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 4.1 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, WHO, NASREA and NAFDAC 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, NASREA and WHO 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. Compared with WHO, FAO, NASREA. 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 Non- Biogenic Heavy Metals in Roadside Soil Samples

Figure 4.6 summarized the mean concentration of some non- biogenic heavy metals across selected roads in urban Kano city. These figure clearly indicates that Pb (1.58mg/kg) and As (0.35mg/kg) have the highest mean concentrations, while Cr (0.10mg/kg) and cd (0.02mg/kg) have the lowest concentrations in all the selected roadside soil samples. Figure 4.7 to figure 4.10 indicates mean concentration of each metal at each selected roadside. **Lead (Pb),**Figure 4.7 shows the distribution of lead in the soil samples analyzed with the concentrations ranged from 0.08 to 1.59 mg/kg. Lead was detected in all the six sampling areas with the highest concentration value of lead (1.59 mg/kg) in KTN sampling area, followed by KRW, KNL and HDJ. While GRA has the lowest concentration lead value of (0.08 mg/kg). According to world health organization (2007), the permissible level of Pb for urban soil is 10mg/kg (Devi *et al.,* 2014). None of the samples site exceeds this limit. This indicated there is a definite contamination which is contributed by the vehicular emission to the soil along the roads. In a similar study, Ayateye *et al.,* (2009) reported a concentration of lead (Pb) in roadside soil levels ranges from 16 to 20 mg/kg. The result of this study reveals that the content of lead (Pb) in roadside soil is higher than the acceptable limits. The elevated level of lead (Pb) may cause the toxicity and potential health hazards to those residing closed to the roads sides. Pb exposed can result in weakness of the joints, failures of reproduction, nausea and loss of memory (Asio, 2019).ANOVA results showed that there was significant difference among the lead obtained from the six sampling location (p=<0.05). **Cadmium (Cd),** The mean concentration of cadmium levels in all the roadside soil of urban Kano were in the safe zone, they ranged between 0mg/kg to 0.03mg/kg (figure 4.8) compared with the maximum permissible limits of WHO (2000) (10mg/kg) FEPA (2000) (3.6mg/kg) and EU (2002)(3mg/kg) (Devi *et a.l,* 2014). Cadmium in soil may cause threat to human and animals in the near future, although the tear of tyres may be recognized as major sources of Cd along roads sides (Hardy *et al*., 2008). Generally the levels of cadmium obtained in KTN and KRW compared to the levels of other heavy metals in the roadside soil could be attributed to the high mobility of Cd through the soil layer. Cd is likely to be more mobile in soil system than other heavy metals (Adelekan and Abegunde 2011).

High levels of Cd exposure may lead to severe pains in the joints, bone disease, kidney and lung problems (Hardy *et al.,* 2008). Also Cd exposure can lead to situation such as neutrotoxin, hypertension, carcinogenic, liver dysfunction, nausea, vomiting, respiratory difficulties and loss of conscious (Adelekan and Abegnde, 2011; Bhasure and Mirgane, 2011). ANOVA results showed that there is highly significance among the cadmium results obtained from the six sampling locations (p=<0.05). **Arsenic (As),** The mean range concentration of arsenic in the roadside soil samples was 0.19mg/kg to 0.40mg/kg.(Figure 4.9) shows that the highest Arsenic (As) concentration in the roadside soil was observed at NYL (0.40mg/kg), followed by GRA (0.35mg/kg), KNL (0.34mg/kg), HDJ (0.30). KTN (0.24mg/kg) and KRW (0.19mg/kg) has the lowest concentration of As, the accumulation of As in soil can be related to industrial activities and the used of sprays, Arsenic (As) compounds are used as pesticides. The results do not exceed the maximum permissible limit of 20mg/kg according to W.H.O. (2000).ANOVA results shows that there was significant difference between the arsenic obtained from the six sampling locations (p=<0.05). **Chromium (Cr),** The chromium levels in all the roadside soil of urban Kano were found in trace amount between 0mg/kg to 0.10mg/kg,(figure 4.10) compared with the maximum permissible limits of WHO (2002),(100mg/kg), the roadside soil of NYL and GRA were not contaminated with chromium, it's probable that anthropogenic activities were negligible, its source seems to be neutral, the Cr contents obtained in this study ranged from 0.00-0.19 mg/kg, the highest concentration was found in KRW soil samples with the concentration of 0.10 mg/kg, GRA and NYL was not contaminated with the Cr among the samples.

Chao *et al*., (2010); Payus and Talip, (2014) have shown lower concentrations of 0.07mg/kg, 0.9mg/kg respectively compared to this study. The range of 0.00 – 53.89mg/kg were reported by Ihediola, *et al*., (2013) for roadside soil samples from Enugu, Nigeria, Yap *et a*l., (2009) recorded 1.32mg/kg - 0.24mg/kg content of Cr in the soil samples from Malaysia, the values are in accordance with the results obtained in this study.

The concentration of Cr in the roadside soil samples analyzed was lower than the maximum permissible limit of 2.3mg/kg by FAO, (2001) and WHO (2001). There were significant differences (P=<0.05) in the level of Cr determined as reported by ANOVA.

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 4.2) 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. The pollution level for Pb (I_{geo}=5.02 to 3.06) showed that KTN highway soil was fond to be strongly contaminated, that of KRW, KNL and HDJ were found to be strong to moderate, strong contaminated and that of NYL was found to be moderate contaminated while GRA was found to be uncontaminated to moderate.(table 4.3) For Cr and Cd (I_{geo}=0.00) shows that there was practically uncontaminated, 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 4.2 Geoaccumulation index (I_{geo}) of heavy metals in the highways roadside soil

Location	Pb	Cr	Cd	As
GRA	1.26	0.00	0.00	0.00
KTN	5.02	0.00	0.00	1.35
KNL	3.06	0.00	0.00	1.03
KRW	4.02	0.00	0.00	1.02
NYL	2.00	0.00	0.00	1.02
HDJ	3.03	0.00	0.00	1.03

Table 4.3: 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 non-biogenic heavy metals (Pb, Cr, Cd and As) 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 Non-Biogenic metals (Pb, Cr, Cd and As) concentrations in roadside soil samples appeared to have a low level of contamination. KRW, KTN and KNL appeared to have a high level of Pb, Cr and Cd. 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 followig

1. Concentrations of other heavy metals in the roadside soil samples of the sampling areas should be constantly monitored.
2. 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.

3. 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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