



Distribution of Some Biogenic and Non-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) and non-biogenic (arsenic, cadmium, chromium and lead) trace 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 Bouyous. 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 microkjeldhal digestion method. Available phosphorous was determined using Bray 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 phenolphthalein as indicator. Exchangeable bases (Ca, Mg, K and Na) of the soils were extracted using 1N neutral ammonium acetate (NH₄OAC) and Ca, Mg, Cr, Cd, Pb, As, Cu, Zn, Fe, Mn and Ni were determined using Microwave Plasma Atomic Emission Spectroscopy (MPAES machine). The biogenic trace metals were evenly distributed in the Roadside soil, whereas the pattern for non-biogenic metals was not consistent. The results of biogenic metals were lower than the limits set by the Swedish Environmental Code, NASREA, SON and WHO. Whereas some of the non-biogenic metals were close to the limits. 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. More investigations are justified to verify these risks.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the Study

The terms "Bio" means life or associated with life, the term biogenic means essential for maintaining the fundamental life processes, Biogenic trace 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 depends 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 (As), Nickel (Ni) and Wolfram (W). The role of trace 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).

1.2 Heavy Metals

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).

1.2.1 Sources of Heavy Metals in Contaminated Soil

Largely, within the European community the eleven elements of highest concern are arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin, and thallium. Metals occur naturally in our environment, but rarely at toxic levels, especially in the Earth's crust, where they contribute to the balance of the planet (Harikumar *et al.*, 2010; Obodai *et al.*, 2011; USDA and NRSC, 2000). Generally, metals enter the aquatic environment through atmospheric deposition, erosion of geological milieu or due to anthropogenic activities caused by industrial effluents, domestic sewage and mining waste (Adelekan and Abegunde, 2002; Aderinola *et al.*, 2009; Bhagure and Mirgane, 2010; Ene *et al.*, 2009; Obodai *et al.*, 2011). Heavy metals are always present at background levels of non-anthropogenic origin where their source in soils could be related to weathering of parent rocks and pedogenesis. Heavy metals occur naturally in the ecosystem with large variations in concentration

1.2.2 Properties of Heavy Metals

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; Suci *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).

1.2.3 Effects of Heavy Metals

Heavy metals can be described as contaminants in the soil environment because (i) through man-made cycles their rates of generation are more rapid relative to natural ones, (ii) they become transferred from mines to random environmental locations where higher potentials of direct exposure occur, (iii) compared to those in the receiving environment the concentrations of the metals in discarded products are relatively high, and (iv) the chemical form (species) in which a metal is found in the receiving environmental system may render it more bioavailable (Wuana and Okieimen, 2011). Occurring as natural constituents of the earth's crust, heavy metals are by nature non-biodegradable and tend to be contaminants to living things in the environment (Aderinola *et al.*, 2009; Bhagure and Mirgane, 2010; Obodai *et al.*, 2011).

1.2.4 Uses of Heavy Metals

Heavy metals have varied uses, even though in certain concentrations they tend to be dangerous. Some of its uses are as follows:

- Lead is also used in the manufacture of lead storage batteries, solders, bearings, cable covers, ammunition, plumbing, pigments and caulking (Wuana and Okieimen, 2011).
- Copper is also used in the production of blood haemoglobin, seed dressing, disease resistance and regulation of water (Wuana and Okieimen, 2011).
- In small amounts nickel can be used by the body to produce red blood cells and then as an ingredient of steel and other metal products (Asio, 2009; Lenntech, 2010).
- Cadmium compounds are used in re-chargeable nickel-cadmium batteries, pigments, stabilizers for polyvinyl chloride (PVC), alloys and electronic compounds (Järup, 2003; Wuana and Okieimen, 2011).
- Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials (Lenntech, 2010). Chromium is required for carbohydrate and lipid metabolism and the utilization of amino acids (Asio, 2009).

1.3 Urban Soil Contamination

This is a site that has had one or more certain substances added to it exceeding background levels. The product or the substance may exist in the soil, groundwater or surface water at a concentration which presents a risk of harm to human health or the environment (Stavrianou, 2007). The contaminating substances include heavy metals, solvents, medical waste, fuels, acids, asbestos, oils and hazardous waste (Stavrianou, 2007; Worksafe, 2005). Various channels may be used to identify contaminated sites. This includes contamination: on the surface of the soil or in fill material, deeper in the soil (e.g. covered by soil or fill and not exposed until excavation starts), in surface water, in groundwater, in the air, taken up by vegetation growing on the site and as a result of substances released from existing buildings or plant or during demolition (e.g. asbestos) (Stavrianou, 2007; Worksafe, 2005).

1.3.1 Causes of Urban Soil Contamination

Accidental spills of oil

Acid rain

Intensive farming
Deforestation
Genetically modified plants
Nuclear wastes
Landfill and illegal dumping
Agricultural practices
Mining activities
Heavy metals from vehicle brake linings
Automobile exhaust, etc.

1.4 Behavior of Inorganic (Heavy Metals) Contamination in the Soil

The most prevalent group of element in the sub soils is the transition metals otherwise called heavy metals. Examples include Copper (Cu), Iron (Fe), Manganese (Mn), Zinc (Zn), Mercury (Hg), Arsenic (As), Lead (Pb), Nickel (Ni), etc. These metals may occur in soil due to industrial discharge, waste disposal; waste incineration and vehicle exhaust (Bilos *et al.*, 2001; Koch and Rotard, 2001).

1.4.1 Lead (Pb)

Lead is an important metal which is belonging to period 6 and group IV of periodic table having atomic number 82, mass number 207.2, density 11.4g/cm³, melting and boiling point 327.4°C and 1725°C respectively. Lead is bluish gray naturally occurring metal found mostly as mineral combined with various other elements like oxygen(PbCO₃), or sulphur(PbS, PbSO₄), and in earth's crust range from 10 to 30mg/kg(USDHHS, 1999).

Lead is a soft heavy metallic element. It was one of the nine chemical elements known and used in the ancient world. Throughout history it has been widely employed in arts and architecture and in modern times it has been used in making printer typefaces and reaction shields. It is used as element in lead storage batteries, solder, plumbing, cable covering is also recognized. It is used in interior paints. It causes serious hazards because lead is highly toxic if improperly handled (Wajahat *et al.*, 2006).

1.4.2 Chromium (Cr)

The only Chromium compound of practical importance is chromites, a slack spinal of the idealized composition FeCr₂O₄ in practice it contains varying amount of MgO, Al₂O₃ and SiO₂ major producers of chromites include South Africa, Russia, Albania etc. Since 1990, the production of chromites has doubled roughly every decade, reaching 2.6million tones, in 1984; chromium was more rarely as the mineral crocoites (PbCrO₄) and minor amounts minerals.(Hardey *et al.*, 2008).

The greater part of chromites are produced by heating with coal to give ferrochrome used in the manufacture of alloy steels, pure chromium metal for use in iron is produced by reduction of Cr₂O₃.(Asio, 2009)

Chromium is toxic in high concentration to both plants and animals. It causes perforation, bronchogenic, carcinoma etc. Chromium poisoning cause's skin disorder and liver damage. Chromium has a wavelength of 357nm. (Adelekan and Abegunde, 2001).

1.4.3 Cadmium (Cd)

Cadmium is a white shining but tarnishes able metal, similar in several characteristics to Zinc and Tin. Cadmium is not found to a great extent in nature, its presence in the earth crust is estimated to range between 0.15 to 0.11mg/g (67th element in order of abundance), with a Zn/Cd ratio around 250:1 (the ratio depends strictly on the nature of rocks). (Wuana and Okieimen, 2011).

Cadmium can be present as a result of volcanic emission and release from the vegetation. It is not essential to plant growth, but under certain conditions can accumulate in some plants to level that are hazardous to animals and humans. Some sewage sludge contains enough cadmium to encourage accumulation. The chemistry of cadmium reaction in the soil is not well understood, but it is known that the uptake of this element is generally reduced by organic matter, silicate clay, and hydrous oxides of iron and aluminium and poor soil aerations

1.4.4 Arsenic (As)

Arsenic is one of the most important heavy metals causing disquiet from both ecological and individual health standpoints. It has a semi-metallic property, is prominently toxic and carcinogenic, and is extensively available in the form of oxides or sulfides or as a salt of iron, sodium, calcium, copper, etc. (Singh *et al.*, 2007).

Arsenic is the twentieth most abundant element on earth and its inorganic forms such as arsenate and arsenite compounds are lethal to the environment and living creatures. Humans may encounter arsenic by natural means, industrial source, or from unintended sources. Drinking water may get contaminated by use of arsenical pesticides, natural mineral deposits or inappropriate disposal of arsenical chemicals. Deliberate consumption of arsenic in case of suicidal attempts or accidental consumption by children may also result in cases of acute poisoning (Mazumder, 2008).

1.4.5 Iron (Fe)

Iron is the most abundant transition metal in the earth crust. Biologically it is the most important nutrient for most living creatures as it is the cofactor for many vital proteins and enzymes (Hilman, 2001). Iron is an essential element for all forms of life and is non-toxic. The average human contains about 4g of iron. A lot of this is in hemoglobin, in the blood. Hemoglobin carries oxygen from lungs to the cell, where it's needed for tissues respiration. Human need 10-18 milligram of iron each day. A lack of iron will cause anemia to develop. Food such as liver, kidney, molasses, brewer's yeast, cocoa and liquor ice contain a lot of iron. The acute ingestion of iron is especially hazardous to children. In life-threatening toxicity is associated with pediatric ingestion of potent adult preparations, such as prenatal vitamins. Serious iron ingestion in adults is usually associated with suicides attempts. (Sumontha *et al.*, 2006).

1.4.6 Copper (Cu)

Copper is a transition metal which belongs to period 4 and group 1B of the periodic table with atomic number 29, atomic weight 63.5, density 8.96g/cm³, melting point 1083°C and boiling point 2595°C. The metal's average density and concentrations in crustal rocks are 8.1 x 10³ and 55mg/kg, respectively (Davies and Jones, 1988).

Copper is essential to life. It is needed to absorb and utilize iron (Conservation Current, 2005) when it's taken, it leads to the activation of certain enzymes. Copper is non-toxic but its soluble salts are poisonous when they are ingested through misguided or suicidal intent. It is both essential and toxic and may be risks to living, if there is too much in the environment (Scheinberg, 1991),

1.4.7 Manganese (Mn)

Manganese is found in nature (often in combination with iron), and in many minerals (Schroeder *et al.*, 2000). Manganese metal with important industrial metal alloy uses, particularly stainless steel. Manganese phosphating is used as a treatment for rust and corrosion prevention and steel. Depending on their oxidation state, manganese ions have various colors and are used industrially as pigments (Schroeder *et al.*, 2000). The permanganates of alkali and alkaline earth metals are powerful oxidizers. Manganese dioxide (MnO₂) is used as the cathode (electron acceptor) material in standard and alkaline disposable dry cells and batteries (Roth *et al.*, 2013).

1.4.8 Zinc (Zn)

Zinc is an essential trace element involved in major metabolic functions in all living organism. It is found in all human tissues and body fluids (Ohnesorge and Wilhelm, 1991). Zinc is a component of over 300 enzymes needed to repair wounds, maintain fertility in adults and growth in children, synthesize protein, helps in reproduction of cells, preserve vision, boost immunity and protect against free radical (Ohnesorge and Wilhelm, 1991). It is "typically the most second abundant transition metal in organism" after iron and it is only metal which appears in all enzymes classes (Broadley *et al.*, 2007). There are 2-4 grams of zinc (Rink and Gabriel, 2000) distributed throughout the human body. Highest concentration in the prostate and part of eye (Wapnir, 1990).

1.5 STATEMENT OF THE PROBLEM

The distribution of heavy metals in roadside soil is a serious pollution problem in Kano city, because of increase in urbanization, industrial development and agriculture. A control of roadside soil is significant challenge in some Kano city areas and also in the other spheres with high level of vehicular traffic upon highways road like KATSINA ROAD (KTN), KANO LINE ROAD (KNL), HADEJA ROAD (HDJ) NASSARAWA SULTAN ROAD (GRA) AND NAIBAWA ZARIA ROAD (NYL). Therefore scientists needs to investigate the effect of heavy metals in roadside soil in Kano city.

Human beings have been exposed to heavy metals for immeasurable time in virtually every area of modern consumers such as construction material, cosmetics, medicine, processed food, fuel source, personal care product etc, it is very difficult for everyone to avoid exposure to any heavy metals in our environment,(Wang and Zhang, 2018).

1.6 AIM AND OBJECTIVES

The aim of this work is to assess the distribution of some biogenic and non-biogenic heavy metals in roadside soil from selected highways in urban Kano city.

The objectives of this study are to:

- determine the contents of some biogenic and non-biogenic trace metals and some properties of roadside soil within Kano city.
- Provide the scientific basis for the composition of roadside soil as indicator for the influence of traffics residential and commercial activities on the metal contents.
- To sensitize the populace on dangers associated with indiscriminate dumping of waste along roadside in the environment.
- Correlate analyzed samples with existing quality standards

CHAPTER THREE

3.00 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)HNO₃ for 24hrs rinsing three times with deionized water and dried in an oven before used. All operations were performed on a clean laboratory bench.

3.1 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 137Km²and 499Km² 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. .

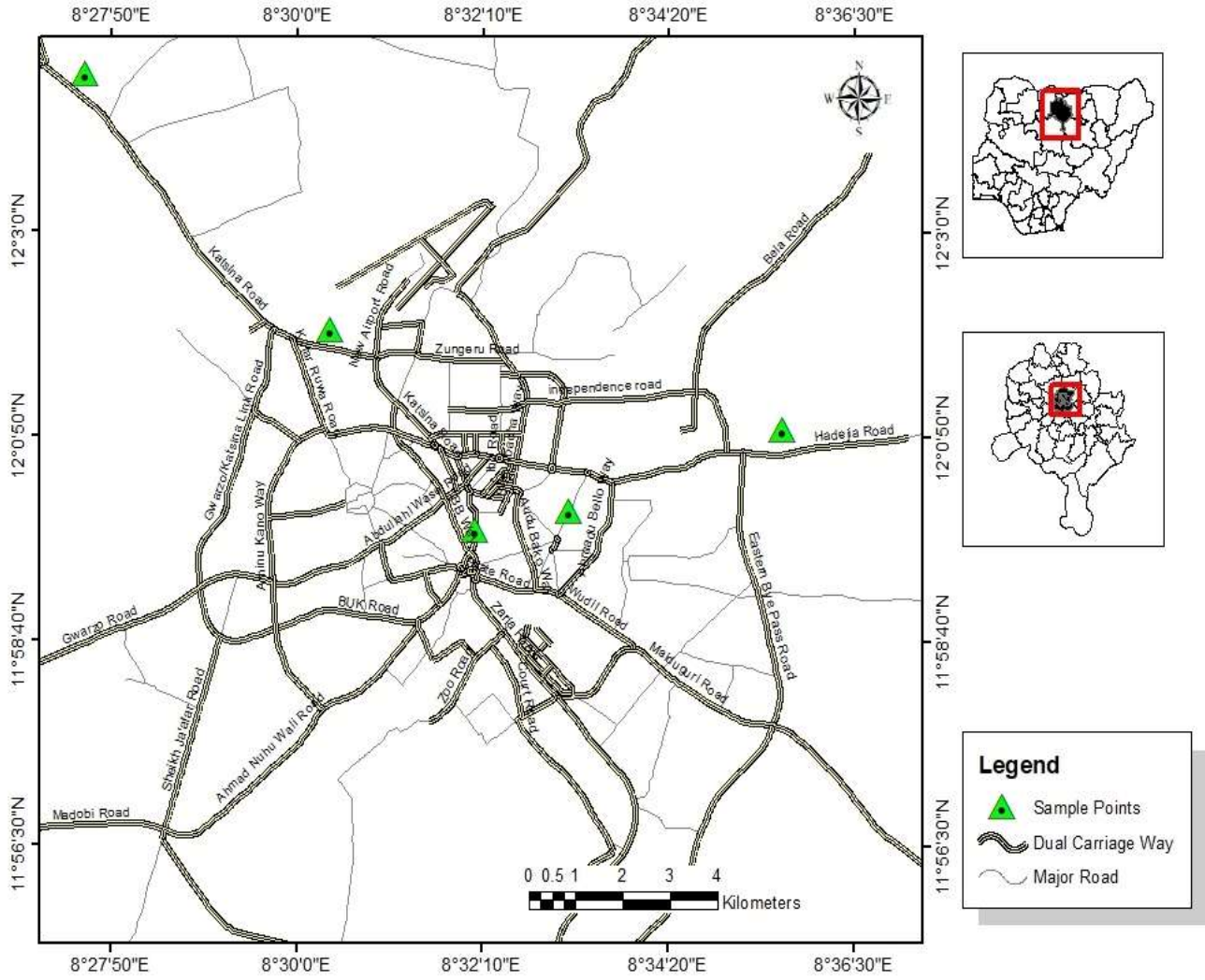


Figure 3.1 Kano metropolis showing the selected roads for the study.

3.2 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 polyethylene 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).

3.3 Preparation of Soil Samples

The entire six soil samples collected were air dried and ground using ceramic 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.

3.4 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.HNO₃ was added. The mixture was boiled gently for 30-45min to oxidize all easily oxidizable matter. After cooling, 5cm³ of 70% HClO₄ was added and the mixture was boiled gently until white dense 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.

3.5 Physicochemical Parameters of the Soil Samples

3.5.1 Particle Size Determination

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

70g of the soil sample was added successive aliquots into 40cm³ of hydrogen peroxide H₂O₂, until the effervescence of the reaction was minimal. The procedure was performed on an 80°C hotplate. The oxidized samples were placed in a forced-air oven and allowed to dry-off at 80°C. Dispersion was obtained by shaking 50g of dry soil sample with 100cm³ of 25% sodium hexametaphosphate for 16 hours in a reciprocating shaker. The mixture was then placed in a Bouyoucos blender cup and stirred for two minutes with an electrical mixer. The contents of each sample were transferred to a 2L sedimentation cylinder, and the cylinder was filled with deionized water to the 2000cm³ mark. The mixture was then homogenized using manual agitation. Destruction of SOM and dispersion of the sample, the sand was separated from the sample by sieving it through a 53 µm mesh and quantified gravimetrically. Before the hydrometer was used, a blank solution was performed. This consisted of hydrometer readings at 40 seconds and two hours in the same cylinder with dispersant samples and then water without the soil samples.

Sand%=100(volume x 2 blank) x 100/oven-dry wt.

Clay%= (volume x 2 blank) x 100 / oven-dry wt.

Silt % = 100 sand % - clay %

3.5.2 Soil pH

The pH meter was calibrated using three buffers such as buffer pH4, pH7 and buffer pH9, 10g of soil sample was weighed into 100cm³ beaker, and 20cm³ of deionized water was added and allowed to absorb water without stirring. It was then thoroughly stirred for 10 second using glass rod. The suspension was stirred again for another 30 minutes, the pH was recorded using the calibrated pH meter (pH-8414 ph/mVOC meter analytical instrument)(Estefan *et al.*, 2013)

3.5.3 Soil Organic Carbon

Organic carbon was determined by potassium dichromate wet oxidation method of walkley and black (1934). 1g of air-dry soil was weighed into 500cm³ beaker. 10cm³ of 1.0M K₂Cr₂O₇ was added using pipette of concentrated H₂SO₄ was also added using dispenser and the beaker was swirled to mix the suspension. It was allowed to stand for 30minutes. 200cm³ of deionized water was added, followed by 10cm³ of concentrated H₃PO₄ using dispenser, and was allowed to cool. 10-15 drops of diphenylamine indicator was added, a magnetic stirrer bar was added, and placed on a magnetic stirrer. The solution was then titrated with 0.5M(NH₄)₂SO₄.FeSO₄.6H₂O, until the colour changes from violet-blue to green. Two blanks, containing all the reagents but no soil sample was prepared, and was treated exactly the same way as the soil suspension (Estefan *et al.*, 2013).

CALCULATION

$$M = \frac{10}{\text{Volume of blank}}$$

$$\text{Oxidizable Organic Carbon (\%)} = \frac{(\text{Volume of blank}-\text{volume of sample}) \times 0.3 \times M}{\text{Wt of sample}}$$

% Organic matter was calculated by multiplying %organic carbon x 1.72

$$\% \text{ O.M} = \% \text{ O.C} \times 1.72 \text{ (AOAC, 1990).}$$

3.5.4. 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, CH₃CH₂OH was used to bring the electrical conductivity to less than 40mS/cm. to displace the sodium adsorbent, 1.0M NH₄OAc was used. After shaking and centrifuge three times with NH₄OAc, the supernatant was collected through filtration in 100cm³ volumetric flask and made up the volume with NH₄OAc 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).

3.5.5 Analytical Procedure for Heavy Metal Determination

All measurements were performed using an Agilent 4210 MP-AES with nitrogen plasma supplied by Agilent 4107 nitrogen generator. The generator alleviated the need and expense of sourcing analytical grade gases. The sample introduction system comprised of a double-pass cyclonic spray chamber and one nebulizer which allow carrier gas to mix with the sample.

An Agilent SPS 4 auto sampler was used to deliver samples to the instrument, allowing the system to be operated unattended. The instrument operated in a fast sequential mode and featured a Peltier-cooled, CCD detector (charge couple detector). Background and spectral interference could be simultaneously corrected easily and accurately using Agilent's MP expert software.

3.6. Sample Analysis

Standard solutions were run to obtain their standard calibration curves for the examination of As, Cr, Cd, Pb, 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 improved 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.

3.7 Statistical analysis

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

CHAPTER FOUR

4.0 Results and Discussion

4.1 Results

The results of the physicochemical 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 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

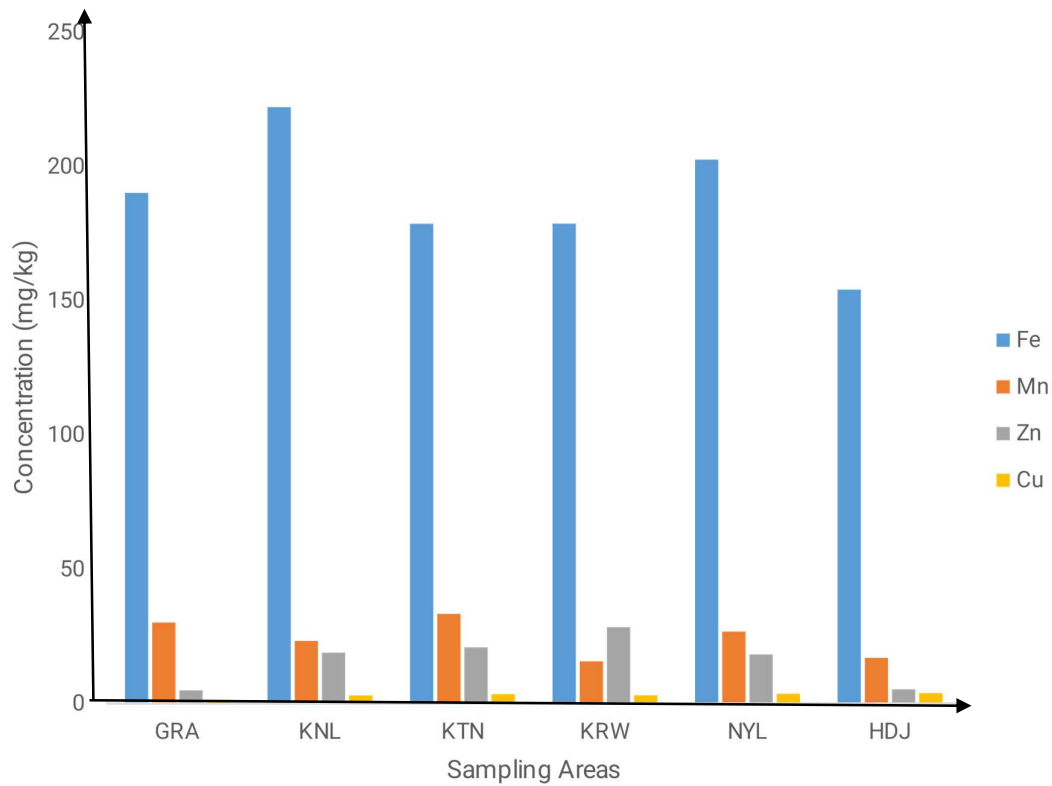


Figure 4.1 Mean concentrations of biogenic heavy metals in roadside soil samples from selected highways in urban Kano city.(mg/kg)

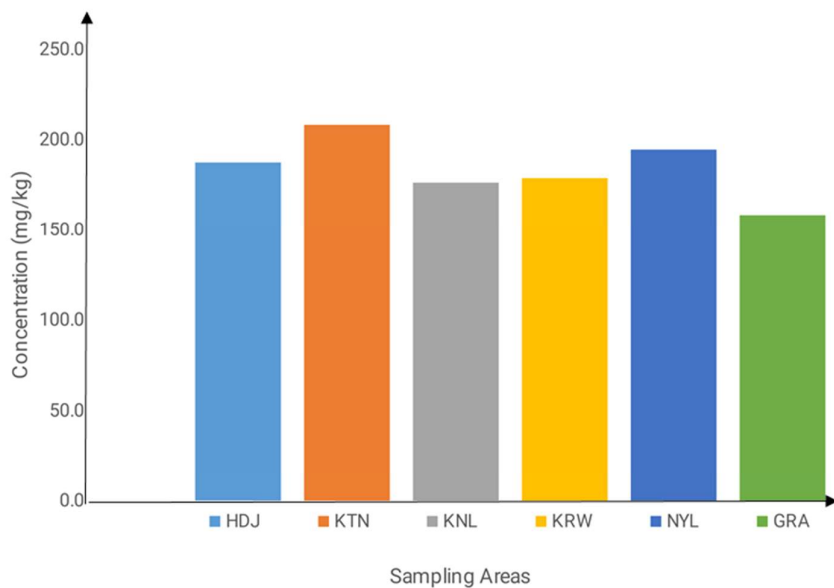


Figure 4.2 Concentration of Iron (Fe) in the soil samples from the sampling areas (mg/kg)

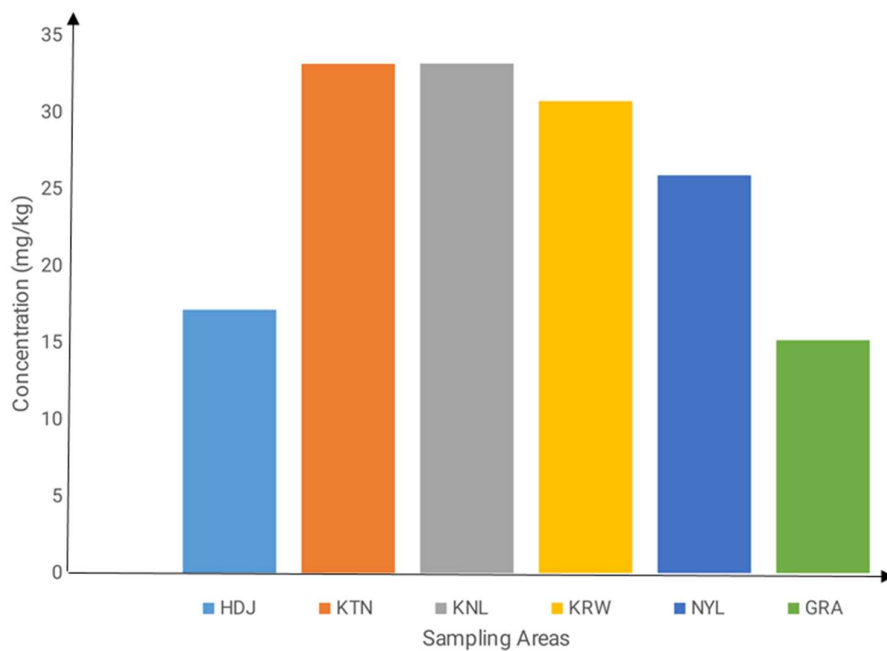


Figure 4.3 Concentration of Manganese (Mn) in the soil samples from the sampling areas (mg/kg)

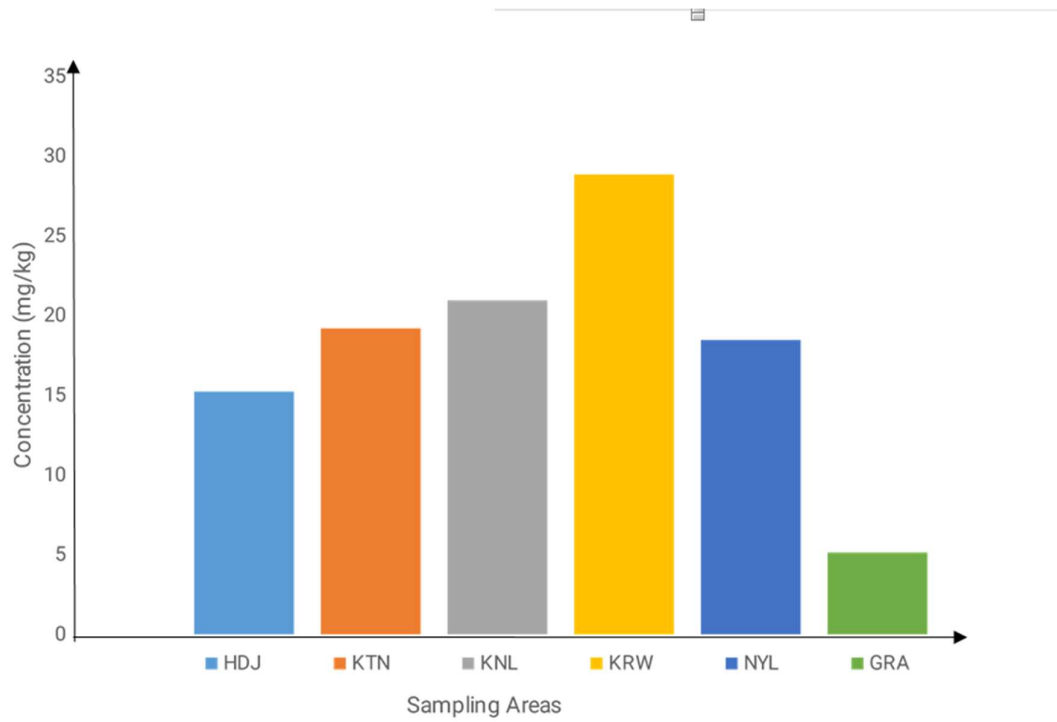


Figure 4.4 Concentration of Zinc (Zn) in the soil samples from the sampling areas (mg/kg)

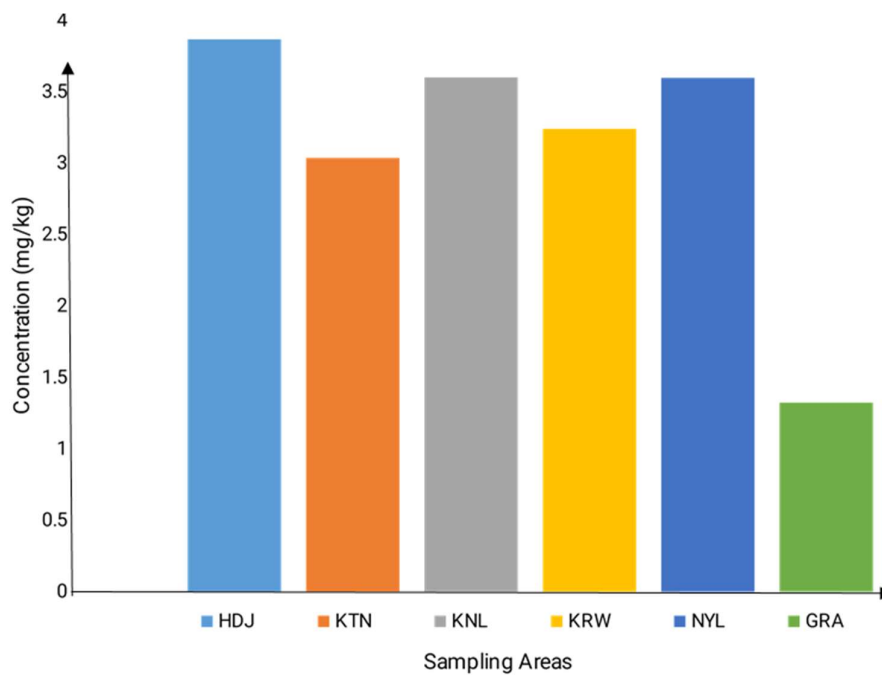


Figure 4.5 Concentration of Copper (Cu) in the soil samples from the sampling areas (mg/kg)

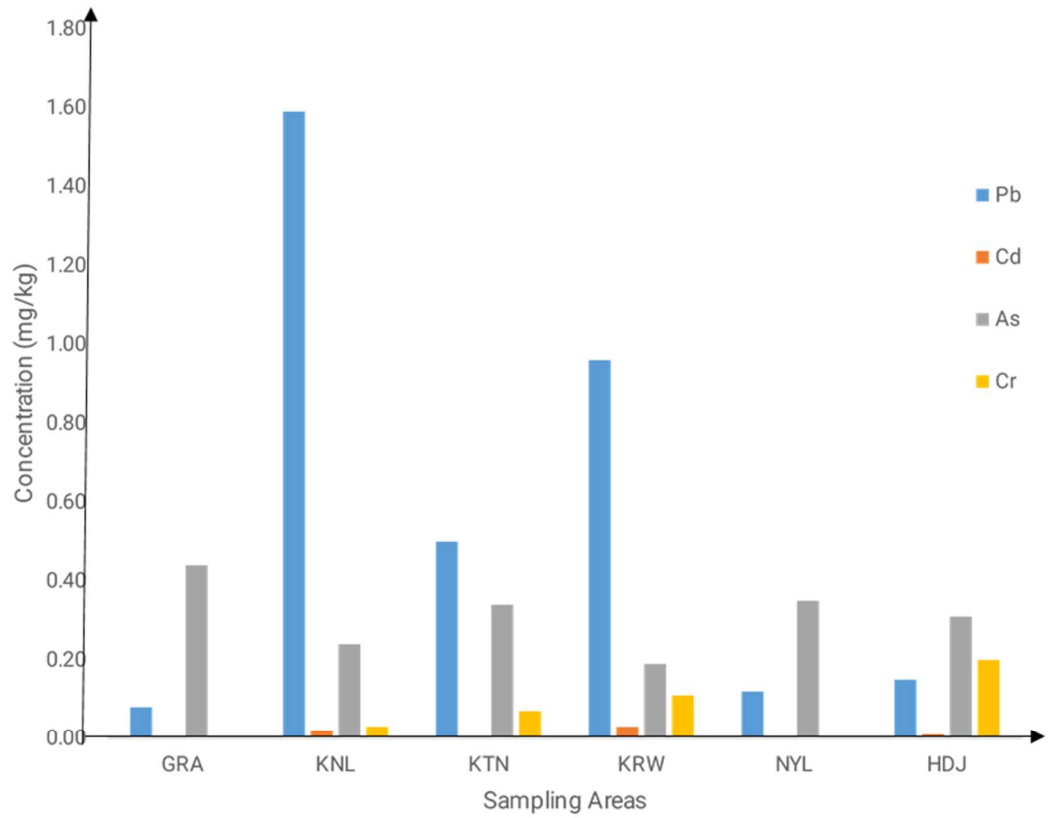


Figure 4.6 Mean concentrations of non-biogenic heavy metals in roadside soil samples from selected highways in urban Kano city. (mg/kg)

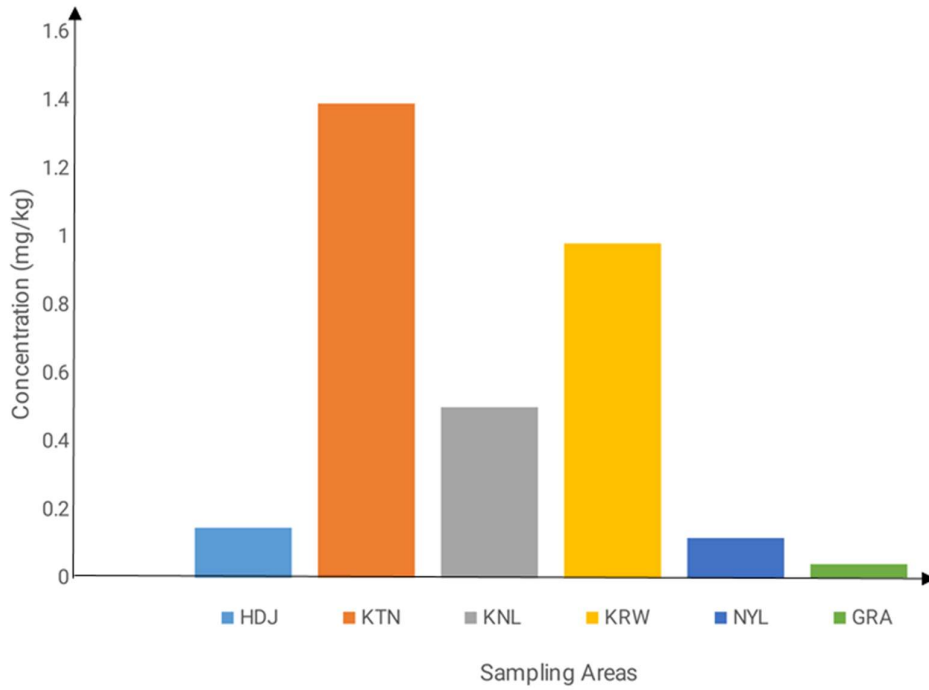


Figure 4.7 Concentration of Lead (Pb) in the soil samples from the sampling areas (mg/kg)

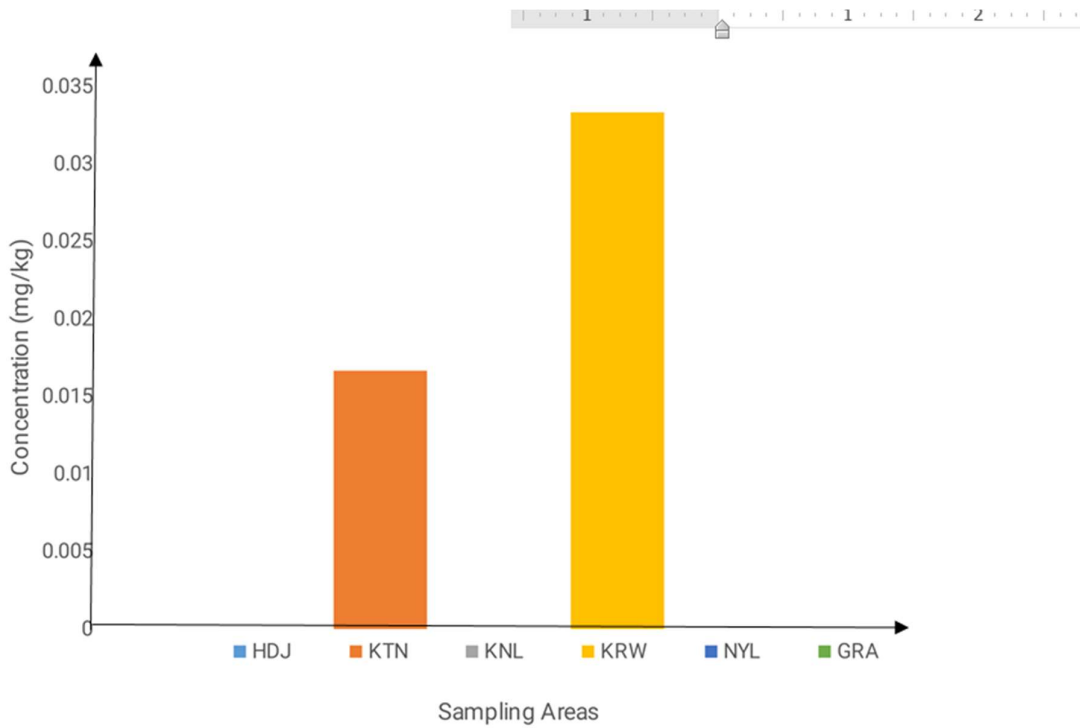


Figure 4.8 Concentration of Cadmium (Cd) in the soil samples from the sampling areas (mg/kg)

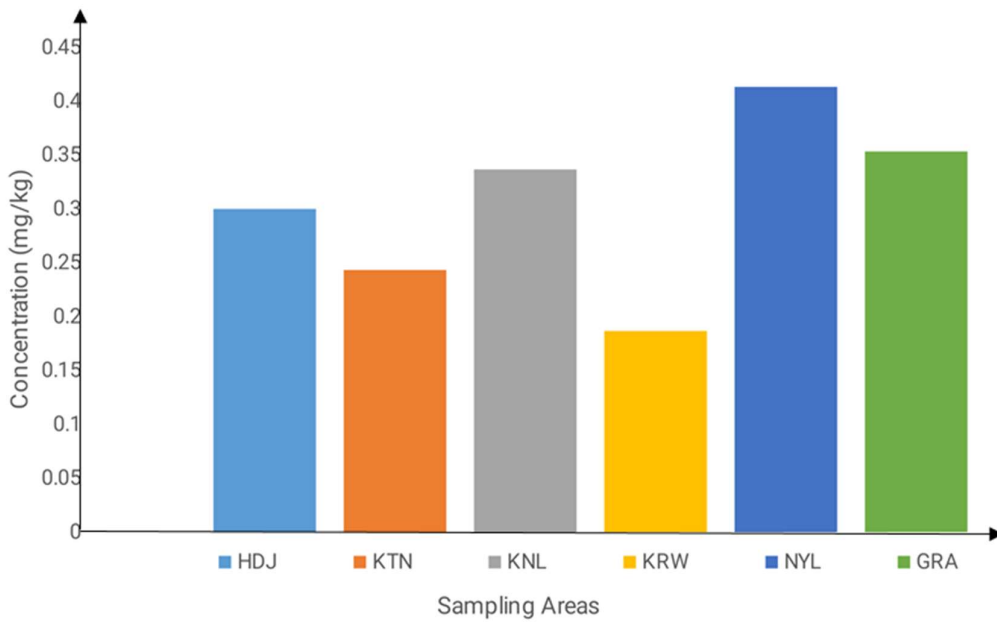


Figure 4.9 Concentration of Arsenic (As) in the soil samples from the sampling areas (mg/kg)

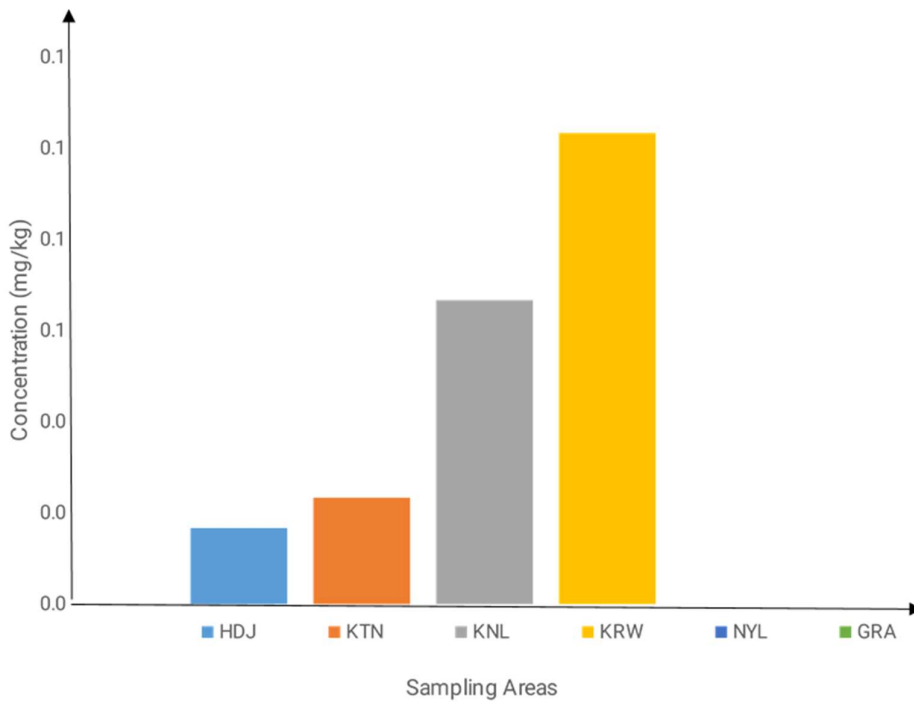


Figure 4.10 Concentration of Chromium (Cr) in the soil samples from the sampling areas (mg/kg)

4.2 Discussion

4.2.1 Physicochemical parameters of the soil samples analyzed

The physicochemical 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 physicochemical characteristics of the soils are summarized in table 4.1 above.

4.2.1.1 pH

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), the moderately acidic soil site may tend to have an increased micronutrient solubility and mobility as well as increases the heavy metal concentration in the soil (Odu *et al.*, 1995). pH is known to be a very unstable soil property that is easily influenced by other properties. Therefore higher release of heavy metals down the horizons to the water soluble could occur when the conditions become favorable such as low pH (Anaka *et al.*, 2009). The pH values of soils obtained from the study is similar with that of 6.10 to 7.0 reported by Shemang, (2016). For determination of some heavy metals in roadside soil and *ablmoachus escuentus* fruit grown near roadside soil in Kafanchan metropolis, Kaduna, Nigeria. ANOVA results showed there was significant difference among the separate mean pH obtained from the six sampling location ($P < 0.05$).

4.2.1.2 Organic Matter

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 conducive 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 physicochemical 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 ($P < 0.05$).

4.2.1.3 Cation Exchange Capacity

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 depends on 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 ($P < 0.05$).

4.2.2 Levels of Some Biogenic Heavy Metals in Roadside Soil Samples

Figure 4.1 summarized the mean concentration of some biogenic heavy metals across selected roads in urban Kano city. These 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 4.2 to figure 4.5 indicates mean concentration of each metal at each selected roadside.

4.2.2.1 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 4.2). 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 ($p < 0.05$).

4.2.2.2 Manganese (Mg)

The mean concentration of Mn in the roadside soil samples ranges between 15.21mg/kg to 33.34mg/kg (figure 4.3) 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 ($p < 0.05$).

4.2.2.3 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 4.4). 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 ($p < 0.05$).

4.2.2.4 Copper (Cu)

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 4.5). 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 ($p < 0.05$).

4.2.3 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.

4.2.3.1 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 ($p < 0.05$).

4.2.3.2 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 al.*, 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 ($p < 0.05$)

4.2.3.3 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 ($p < 0.05$).

4.2.3.4 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 al.*, (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.

4.3 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 found 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	Fe	Zn	Mn	Cu
GRA	1.26	0.00	0.00	0.00	0.01	0.42	0.92	0.78
KTN	5.02	0.00	0.00	1.35	0.02	2.31	1.54	0.69
KNL	3.06	0.00	0.00	1.03	0.34	2.44	1.55	0.86
KRW	4.02	0.00	0.00	1.02	0.31	2.98	1.43	0.70
NYL	2.00	0.00	0.00	1.02	0.14	2.26	1.08	0.18
HDJ	3.03	0.00	0.00	1.03	0.24	2.33	1.04	1.04

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

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

This study shows the presence of some biogenic and non-biogenic heavy metals (Pb, Cr, Cd, As, 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 trace metals determined the soil contained considerable amount of Fe, Mn, Zn and Cu, evenly distributed in the soils. 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 were 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.

5.2 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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