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Source and Distribution of The Heavy Metals: Pb, Cd, Cu, Zn, Fe, Cr, and Mn in Soils of Bauchi Metropolis, Nigeria

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***ABSTRACT** :In this research work the level and distribution pattern of the metals: Pb, Cu, Cd, Cr, Zn, Mn, and Fe were determined in soil of Bauchi Metropolis. Samples were collected from places of high anthropogenic activity such as automobile maintenance workshop (AMW), to places of low activity; the Residential areas (RA). Collection was done from surface to subsurface portion of the soil at the depth of 0 to 15cm at the beginning of raining season in the month of May/June 2017 to late September/October of the same year. Samples were analyzed using Atomic Absorption Spectroscopy (AAS) model AA240FS following digestion with aqua-regia. The results shows that, concentration of Pb ranged from 0.005±0.003 to 0.051±0.002 with highest level from the AMW whereas the lowest comes from the RA and it was not detected in BMP. Level of Cd ranges from 0.002±0.001 to 0.004±0.011, the highest level comes from the AMW, the lowest from the HW, it was not detected in RA and BMP. For Fe, the concentration ranged from 9.559±0.211 to 10.630±0.0231, the highest level was observed along the HW followed by the BMP, the lowest level however comes from the AMW. Cu was only observed in AMW with the level 0.007±0.021. The level of Cr ranged from 0.009±0.005 in the BMP to 0.026±0.003 along the HW. The concentration of Mn ranges from 0.477±0.0121 in the BMP to 0.980±0.121 in the RA. The concentration of Zn ranges from 0.053±0.021 in BMP and RA to 0.252±0.101 in the AMW. All measurements were in ppm. The metals were found randomly distributed within the Metropolis. Flooding coupled with gravity of the rain and the physiochemical property of the soil might have contributed to the level and distribution pattern of the metals within the Metropolis. The research also indicates that, anthropogenic activity is not the main source of the heavy metals but it is additive.*

Keywords :Automobiles, cars, environments, parks, pollution, residential, traffic.

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I. Introduction

Pedos means soil in Greek and the term pedosphere is used to donate the soil cover, the terrestrial part of the earth. Pedology is the science of soil and the method of studying and analyzing it. Soil is the main component of the biosphere, the vital layer of our planet. It is populated by various organisms ranging from tiny bacteria to higher plants, animals and human. It provides the means of physical support for all terrestrial organisms. Presence of heavy metals at elevated levels in the environment may be hazardous to human health. In the urban environment roadside soil has been identified as a sink for heavy metals. Moreover the road side soil is contaminated with heavy metal it can discharge these pollutants into the air and water sectors of the city's environment. It is evident that the urban soil containing the heavy metal pose a serious threat to the safety of the human life by ingestion, inhaling [1] and through the direct contact with the soil on the road sides contaminated by heavy metal [2].

Environmental pollution by heavy metals from road traffics emissions has become a serious issue in the recent past due to their long- term accumulation. Sources of heavy metals in soils in urban environment mainly include; its natural occurrence in the soil derived from parent materials and human activities which are associated with activities such as atmospheric deposition, industrial discharges, waste disposal, waste incineration, urban effluent, long-term application of sewage sludge, fertilizer application in soil, and vehicle exhausts [3, 4]. In many cities in the developing countries in the world, especially in Africa, Nigeria in particular, lack of access to land make many places to be used as garages, parks, including places such as road verges, and any other spot that motorist could occupy. All setbacks along major highways are occupied by motorist and the alarming rate at which this is going is unprecedented. The traffic source of pollutants includes vehicles tire wear, brake linings, fuel combustion, etc. [5] and road infrastructure such as pavement wear, corrosion of galvanized steel, crash barriers, etc. It has been reported that the pollutants such as As, Cd, Cr, Cu, Pb and Zn due to traffic density are mostly found at high levels in soils at sites closer to the roadside that can even affect the environmental air quality [6].

These heavy metal pollutants, derived from a growing number of diverse anthropogenic sources, have had enormous impact on different ecosystem [7]. In urban areas, heavy metals in the roadside soils can be accumulated in human body via direct inhalation, ingestion and dermal contact absorption [8]. The majority of the heavy metals are toxic to the living organism and even those considered as essential can be toxic if present in excess. Excess heavy metals therefore can impair important biochemical process posing a threat to human health, plant growth and animal life [9]. Reports have shown that such pollutants can be harmful to the roadside vegetation, wildlife and the neighboring human settlements [10]. A number of studies have indicated that such metals could be stored in fatty tissues of human beings and consequently affect the functions of the vital organs and disturb the nervous system and endocrine system [11]. Diseases related to high level of heavy metal in the system include lung tissue damage, respiratory illness, liver and kidney failure and others [12]. Cr for instance is carcinogenic and can lead to nasal septum perforation, asthma and liver damage, whereas Ni has been reported to cause nasal and lung cancer [13]. This paper is aimed at determining the level and distribution pattern of the heavy metals; Pb, Cu, Cd, Co, Zn, Cr, Fe, Ag and Mn in soils within Bauchi Metropolis, Nigeria.

II. Materials and Methods

2.1 Sample and sampling sites

Samples were collected from some selected areas within Bauchi metropolis. Four different sampling sites were designated for this study, these include: Bus stop or Motor Park parks (BMP) such site include; Awala round about bus stop, Eagle round about bus stop and NNPC round about Yelwa bus stop; Bauchi Old Motor Park, Jos Motor Park (Jos-Bauchi road), Muda lawal Motor Park (Sultan Abubakar road) and Yankari Motor Park (Bauchi - Gombe road) (Fig. 1). The Highways (HW) this site includes; Ahmadu Bello Highway (Eagle roundabout - Wunti round about), Murtala Mohammed way and Kobi road (Fig. 2). Automobile Maintenance workshops (AMW), this include Dan Gombe mechanical workshop along Jos road (Fig. 3). The Residential areas (RA), this site covers the Government Reservation Areas (GRA) along sokoto road, Bauchi state (Fig. 4). The sites represent areas of high anthropogenic activities (automobile maintenance workshops, car parks, and highways) as well as areas of less or lower activity (the residential areas).

Five different samples were collected at each sampling site. Samples were collected from the surface to subsurface portion of the soil at the depth of zero to fifteen centimeters and at the intervals of two meters apart using hand trowel. All collections were done at the beginning of raining season in the month of May/June 2017 and at the end of the season; late September/October of the same year 2017. These periods are period characterized with less rainfall, no sandstorm and therefore no infiltration of particulate matter other than those within the metropolis. However there were periodical heavy rainfall and flooding these period Samples collected were homogenised and preserved in an acid prewashed cleaned polyethylene bags for subsequent analysis.

2.2 Sample preparation and analysis

Composite samples collected were homogenized, dried at 105°C to a constant weight, ground into fine powder using an acid prewashed mortar and pestle and sieved through a 2mm nylon sieve [9]. Analysis was done using Atomic Absorption Spectroscopy (AAS) model AA240FS following digestion with 10 ml Aqua regia [14] in a digestion tube, for the level of the metals: Pb, Cd, Fe, Cu, Cr, Mn, and Zn in the soil samples.

2.3 Statistical data handling

All statistical data handling were performed using SPSS 17 package. Differences in heavy metal concentrations among the different sites of sampling were detected using One-way ANOVA, followed by multiple comparisons using Turkey tests. A significance level of ($P \leq 0.05$) was used throughout the study.

III. Result and Discussion

`Heavy metals are a group of widespread pollutants in the environment that mostly originate from traffic emission, industrial activities, domestic emission and weathering of buildings and pavements [15]. Although some natural activities result in the release of heavy metals in the environment, report has it that, human activities contributed most to the release metals in the ecosystems [16]. Table one shows the level and distribution pattern of the metals; Pb, Cd, Fe, Cu, Cr, Mn, and Zn determined in the soil samples collected within Bauchi Metropolis, Bauchi state, Nigeria. Of all the elements determined iron (Fe) has the highest concentration. Its level ranged from 9.559ppm - 10.630ppm with the highest level of 10.630ppm ±0.231 from the highways followed by the car or motor parks (10.121ppm ±0.121), the residential area (10.090ppm±0.221) and the least concentration of 9.559ppm ±0.211; however was found in the automobile maintenance workshop (AMW). Next to iron is manganese (Mn) having the highest level of 0.980ppm±0.0121 from the residential areas (RA) followed by the highways (HW) with the concentration of 0.771ppm ±0.130, the automobile maintenance workshop (AMW) has 0.058ppm whereas car or motor parks (BMP) had the lowest concentration of 0.477ppm. The highest level of zinc (0.252ppm ±0.101) was observed in the AMW followed by the HW which has 0.058ppm ±0.120 whereas the level, 0.053ppm ±0.021 was found in BMP and 0.053ppm±0.002 in RA. The elements, Co and Ni were not detected in all the samples from the four sampling sites (AMW, HW, RA and BMP). The level 0.007ppm was observed in the samples from AMW for copper (Cu), however the metal could not be detected in the samples from HW, RA, and BMP. Cadmium one of the dangerous elements with no known biological importance was found in the samples from the AMW and HW with the levels; 0.004ppm ±0.011 and 0.002ppm ±0.001 respectively. However, the element could not be detected in the samples from the RA and BMP. Lead (Pb) another toxic element that as no biological importance to either plant, was found in the samples from AMW, HW and RA with the levels; 0.051ppm ±0.002, 0.006ppm ±0.001 and 0.005ppm ±0.003 respectively. The element was not detected in the samples from the BMP. Chromium was found in the samples from all the sampling sites with the highest level of 0.026ppm±0.003 from HW followed by AMW (0.018ppm ±0.011) then the residential area (0.016ppm ±0.0121), the least level of 0.009ppm ±0.005 was found in the sample from the car or motor park.

The levels and side effect of heavy metals assessed by the analysis of urban soils are still on the rise. This could be probably attributed to the potential public health risk associated with intake of heavy metals. In urban area, heavy metals in urban road or street soils can be accumulated in human body by direct inhalation, ingestion and/or dermal contact absorption [17, 18].The pollution of soils by heavy metals from automobile source is a serious worldwide environmental issue. These metals are released during different operations of the road transport such as combustion, component wear, fluid leakage and corrosion of metals. Lead, cadmium, copper and zinc are the major metal pollutants of the roadside environments and are released from burning of fuel, wearing out of tires, leakage of oils, and corrosion of batteries and metallic parts such as radiators etc. [19. It has also been vastly documented that rapid industrialization, increasing vehicular traffic and application of fertilizers result in the release of large quantities of metals in the biosphere [20].

3.1 IRON (Fe)

Iron is the fourth most abundant element and second most abundant metal in the Earth's crust (after aluminium). It is a major element in soil with a median value of 2.1% [21]. It is present mostly as Fe^{2+} in ferro-magnesian silicates, such as olivine, pyroxene, amphibole and biotite, and as Fe^{3+} in iron oxides and hydroxides, as the result of weathering. The reactions of Fe in weathering processes are dependent largely on pH-Eh, and on the oxidation state of the Fe compounds involved [22]. In soils, Fe is believed to occur mainly in the forms of oxides and hydroxides as small particles or associated with the surfaces of other minerals. However, in soil horizons rich in organic matter, Fe appears to be mainly in a chelated form. The geochemistry of Fe is very complex in the terrestrial environment and is largely determined by the easy change of its valence states in response to the physicochemical conditions. The behavior of Fe is closely linked to the cycling of O, S, and C. The reactions of Fe in processes of weathering are dependent largely on the Eh-pH system of the environment and on the stage of oxidation of the Fe compounds involved. The general rule governing the mobilization and fixation of Fe are that oxidizing and alkaline conditions promote the precipitation of Fe, whereas acid and reducing conditions promote the solution of Fe compounds [23]. A high rate of Fe mobility in soils under anthropogenic stress (acid rain, acid fertilizers, high input of organic matter) may affect an increase of Fe mobility in various hypergenic zones. In consequence, the accumulation of Fe in certain horizons of different soils may significantly change the geochemical cycling [24].

The Fe compounds that are produced are largely responsible for the color of soils and have been used for the description of soil processes and for soil classification. In this study, iron was found at a higher level than all the elements determined and in all the samples from all the sampling sites. The anthropogenic sources of iron have been reported to include the iron and steel industry, sewage and dust from iron mining [25]. Iron sulphate is also used as a fertilizer and herbicide [26]. There are no such sources or industries in Bauchi metropolis, therefore the high level of iron in the metropolis could mostly be attributed to natural soil derived source especially the high level of the metal observed in the residential area which was found higher than what was found even in the AMW (Table 1). Though the level of iron observed in this study was high especially in the samples from the residential areas, it is many-fold lower than what was observed in Mubi and Enugu by Shingu et al. [27] and Ekere and Ukoha, [28]. The level observed in samples from the residential area of this study is however higher than what was observed in the samples from residential areas of some part of Lagos

[29]. Iron (Fe) levels in all the samples from the sampling sites within the Metropolis of this study were lower than what was observed in Gubi town [30].

3.2 CHROMIUM (Cr)

Chromium is a lithophile metallic element forming several minerals, including chromite $FeCr_2O_4$ and the rare crocoite $PbCrO_4$, and is present as an accessory element in several others, such as spinel, amphibole, mica, pyroxene and garnet. Most of the Cr^{3+} is present in the mineral chromite ($FeCr_2O_4$) or in other spinel structures, substituting for Fe or Al. In general, Cr^{3+} closely resembles Fe^{3+} and Al^{3+} in ionic size and in geochemical properties. Chromite, the common Cr mineral, is resistant to weathering and therefore accounts for most of the Cr in residual material. However, under progressive oxidation, Cr forms the chromate ion (CrO_4^{2-}), which is readily mobile and also is easily sorbed by clays and hydrous oxides [23].

Major sources of Cr are Air conditioning coolants, Engine parts, Brake lining, catalytic converters, wear and tear of chrome plated vehicular parts, yellow paints on the roads used for marking and metal industries [31, 32]. Other sources of chromium in soils are from industrial waste originating from the tanning, chemical, metallurgy, cement and asbestos industries [33], in which chromium exists under hexavalent forms: chromate (VI) and dichromate (VI) ions, as well as in trivalent forms. In most soil samples the Cr concentrations were lower than the world median content of this element which is estimated to be 54 mg kg^{-1} [34]. In this study the level or concentration of Cr ranged from 0.009ppm in the car or Motor Park to 0.026ppm on the highways. This concentration was found lower than what was observed in Gubi town [30], Mubi [27], some selected motor parks in Lagos [29], Fallujah city in Iraq [35]. Higher speeds reached by cars mean that both tires and road surfaces are worn out faster, which adds to a higher content of elements in roadside soil. According to Helmreich et al. [36], apart from the traffic flow rate, another factor which affects the accumulation of contaminants in soils near roads is the weather, namely prolonged periods of drought as well as the duration and intensity of precipitations. All the above factors may have contributed to the elevated concentrations of not only chromium but the trace elements detected along the highways.

3.3 CADMIUM (Cd)

Cadmium is a low-abundance, chalcophile element that most commonly occurs as a substitute for Hg, Cu, Pb and Zn in sulphide minerals, especially sphalerite (ZnS), and, to a lesser extent, in other Zn minerals such as smithsonite ($ZnCO_3$). It is also found in trace amounts in some silicate minerals, such as biotite and amphibole. Cadmium occasionally forms minerals in its own right, most notably greenockite (CdS), but also the rarer octavite ($CdCO_3$) and monteponite (CdO) [25]. There is growing environmental concern about Cd as being one of the most ecotoxic metals that exhibit highly adverse effects on soil biological activity, plant metabolism, and the health of humans and the animal kingdom. The behavior of Cd in the environment and related health aspects has recently been reviewed by Kabata-Pendias and Pendias, [37] and Stoeppler, [38].

The average content of Cd in soil varies between 0.06 to 1.1 mg kg^{-1}, whereas the global mean for surface soil has been estimated to be 0.53 mg kg^{-1}, and apparently all higher values may reflect anthropogenic influences [23]. The level of the Cd in the soil within Bauchi Metropolis of this study ranges from 0.002ppm in the highways to 0.004ppm in the automobile mechanical workshops. These levels are lower than what was found in Maiduguri Metropolis [39], Enugu [28], Mubi [27], Jos Metropolis [40], Ota [41], Dubai [42] and Fallujah city in Iraq [35].

The most significant use of Cd is in Ni/Cd batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance, and high tolerance to physical and electrical stress. Cadmium coatings provide good corrosion resistance coating to vessels and other vehicles, particularly in high-stress environments such as marine and aerospace. Other uses of cadmium are as pigments, stabilizers for polyvinyl chloride (PVC), in alloys and electronic compounds. Cadmium is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products [43]. Cadmium is produced as an inevitable byproduct of Zn and occasionally lead refining. The application of agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils [44].

In industrialised countries there is concern over anthropogenic accumulations of Cd in the environment, and it is classified as a potentially harmful element with respect to soil biological activity, plant metabolism and the health of humans and animals [23]. Cadmium has no essential biological function. It is toxic to humans through the inhalation of dust, causing lung damage, and may cause cancer from long-term exposure [45]. The maximum tolerable intake of Cd is regarded as 7µgkg^{-1} of body weight [45]. Cadmium in the body is known to affect several enzymes. It is believed that the renal damage that results in proteinuria is the result of Cd adversely affecting enzymes responsible for reabsorption of proteins in kidney tubules. The major threat to human health is chronic accumulation in the kidneys leading to kidney dysfunction. Food intake and tobacco smoking are the main routes by which Cd enters the body [46].

3.4 ZINC (Zn)

Zinc is a chalcophile metallic element and forms several minerals, including sphalerite (ZnS), the commonest Zn mineral, smithsonite ($ZnCO_3$) and zincite (ZnO), but is also widely dispersed as a trace element in pyroxene, amphibole, mica, garnet and magnetite [47]. Zinc (Zn) content in soil depends on the nature of parent rocks, texture, organic matter and pH, and ranges from 10 to 300 mg kg^{-1} [48] with an estimated global average of 64 mg kg^{-1} [23]. The different forms of Zn in soil may include: (1) water soluble; (2) exchangeable and extractable from soil surfaces; (3) occluded by soil hydrous oxides; (4) precipitates; (5) immobilised in living organisms and biological residues, and (6) constituents in the lattice of primary and secondary minerals [48]. Several soil profile studies have shown that extractable Zn generally decreases with depth, and since it is easily adsorbed by mineral and organic components in most soil types, it normally accumulates in the surface horizons [23]. Zinc occurs naturally in soil (about 70mg kg−1 in crustal rocks) [49], but Zn concentrations are rising unnaturally, due to anthropogenic additions. Most Zn is added during industrial activities, such as mining, coal, and waste combustion and steel processing. Zn compounds are used extensively as anti-oxidants and as detergent/dispersant improving agents for motor oil. Huhn et al. [50] have identified vehicle brakes and tire wear as possible sources of Zn. The level of Zn in this study varies greatly and in accordance to the degree of activities taking place at a given sites. For instance the automobile maintenance workshop AMW (Figure 1a and b) was found to have the highest concentration of, 0.252ppm Zn. However this concentration was found lower than what was observed in Gubi town [30], Mubi [27], Jos Metropolis [40], Maiduguri Metropolis [39], some selected motor parks in Lagos [29], Fallujah city in Iraq [35] and Faisalabad-Pakistan [51]. The level of Zn observed in this study was higher than what was found in Botswana [52]. The differences in concentration may be attributed to the seasonal variation in the periods of sample collection as well as activities taking place and/or traffic density. The major sources of Zn has been reported as Tire wear, Motor oil, Grease, Brake emissions, Corrosion of galvanized parts [53, 54].

3.5 LEAD (Pb)

Lead belongs to group 14 of the periodic table, which also includes C, Si, Ge and Sn. Lead has the most metallic characteristics of this group. The element has an atomic number of 82, an atomic mass of 207, two oxidation states (+2 and +4) and four naturally occurring isotopes (^{204}Pb,^{206}Pb,^{207}Pb and ^{208}Pb), of which ^{208}Pb is the most abundant at 52% of the total mass. Lead is the most abundant of the transition metal elements [55]. The terrestrial abundance of Pb indicates a tendency for Pb to concentrate in the acid series of magmatic rocks and argillaceous sediments in which the common Pb concentrations range from 10 to 40 ppm, while in ultramafic rocks and calcareous sediments its range is from 0.1 to 10 ppm. The average abundance of Pb in the Earth's crust is estimated at about 15 ppm. The natural Pb content in soil is, of course, related to the composition of the parent rock. Although the species of Pb vary considerably with soil type, it is mainly associated with clay minerals, Mn oxides, Fe and Al hydroxides and organic matter. In some soil types, Pb may be highly concentrated in Ca carbonate particles or in phosphate concentrations. A baseline Pb value for surface soil on the global scale has been estimated to be 25 mg kg^{-1}; levels above this suggest an anthropogenic influence [23]. In this study the levels of Pb ranged from 0.005ppm in the residential areas (RA) to 0.051ppm in the automobile mechanical workshops (AMW). This level however, is lower than what was observed in Maiduguri Metropolis [39], Enugu [28], Mubi [27], Jos Metropolis [40], Ota [41], Dubai [42] and Fallujah city in Iraq [35]. The level of contamination in this study could be arranged in the following order; AMW > HW > RA > BMP. The level of contamination is in accordance to the degree of activities taking place. For in the mechanical workshops, welding, panel beatings, iron filings and paintings, coupled with oil spillage and incessant emissions may contribute to the high level of the metal. Along the highways, speed, density of vehicle, tear and wear of tires, emissions coupled with attrition and abrasion of brake parts as well as high temperature may be attributed to the high level of heavy metals. Reports has it that, metalliferous mining (especially sulphide ores), metallic detritus, Pb-bearing glass and pottery glazes, batteries, old lead-based paints, the corrosion of lead pipes in areas of soft water and sewage sludge are all potential sources of Pb [56].

3.6 COPPER (Cu)

Copper (Cu) in the Earth's crust is most abundant in mafic and intermediate rocks and has a tendency to be excluded from carbonate rocks. It forms several minerals of which the common primary minerals are simple and complex sulfides. These minerals are quite easily soluble in weathering processes and release Cu ions, especially in acid environments. Copper is therefore, considered among the more mobile of the heavy metals in hypergenic processes. However, Cu is a very versatile trace cation and in soils or depositional material exhibits a great ability to chemically interact with mineral and organic components of soil [23]. Typical concentrations of copper in soils range from 14 to 109 mg kg^{-1} being the highest in loamy soils, whereas they are the lowest in light sandy soils [57]. In this present study, the level of Cu ranges from ND to 0.007ppm in the samples from the automobile mechanical workshop. The element was not detected in the samples from the other sampling sites (HW, RA, and BMP). This could be attributed to the season of the analysis being at the beginning of rainfall at this part of the country. Copper is the third most used metal in the world [58]. Reports has indicated that, copper is among the elements released from burning of fuel, wearing out of tires, leakage of oils, and corrosion of batteries and metallic parts such as radiators etc. [19]. These activities are much found in the mechanical workshops and to some extent the motor parks as compare to the residential areas. The level of the metal Cu observed in this study is lower than what was observed in Ota Metropolis, Ogun State, Nigeria [41], many fold lower than what was observed in Mubi and Lagos [27,29], Jos a neighbouring state to Bauchi by Abechi et al. [40], Maiduguri Metropolis, Borno state by Garba et al. [39] and Enugu in south-east Nigeria, by Ekere and Ukoha, [28].

While Cu's interaction with the environment is complex, research shows that most Cu introduced into the environment is, or rapidly becomes, stable and results in a form which does not pose a risk to the environment. It is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. In plants, Cu is especially important in seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. It may also cause increased oxidative damage to lipids, proteins and DNA. Chronic Cu toxicity causes liver cirrhosis and tubular necrosis in the kidney [59, 60].

3.7 MANGANESE (Mn)

Manganese is widely distributed in soils, sediments, rocks, water, ambient air and biological material. World-wide, the average manganese content of soil units varies from 270 (podozols) to 525 mg/kg dry weight (DW) (cambisols); the grand mean calculated for world soils is 437 mg/kg DW [61]. Manganese constitutes approximately 0.1% of the earth's crust, and is a naturally occurring component of nearly all soils [62]. Natural levels of manganese range from less than 2 to 7,000 ppm, with a geometric mean concentration of 330 ppm [63]. Accumulation of manganese occurs in the subsoil rather than on soil surface [62]. An estimated 60-90% of soil manganese is associated with the sand fraction [64]. The behaviour of Mn in soil is very complex and is controlled by different environmental factors, of which pH-Eh conditions are the most important [23]. Under cold climatic conditions, Mn is removed from the weathering zone and soil by acid solutions as bicarbonate or as a complex with organic acids derived from decaying plants. McKenzie, [65] and Bartlett [66] have summarized the present knowledge relating to soil Mn. They stated that Mn is likely to occur in soils as oxides and hydroxides in the form of coatings on other soil particles and as nodules of different diameters. The nodules often exhibit a concentric layering that is suggestive of seasonal growth. Anthropogenic sources of manganese include mining and smelting, engineering, traffic and agriculture. It is also used in the manufacture of steel, glass, dry batteries and chemicals. Permanganate is a powerful oxidising agent and is used in quantitative analysis and medicine. Manganese can be an undesirable impurity in water supplies, forming black oxide precipitates on pipes that may slough off, giving rise to staining, taste and odour problems. Geogenic sources of Mn are generally considered to be much more important than anthropogenic ones in the environment [67]. In this study, the concentration of Mn ranges from 0.477ppm to 0.980ppm. The highest concentration of which was observed in the sample from the residential area. Manganese level in this study is next to Fe (10.630ppm), it is however lower than what was observed in Jos [40], many lower than what was observed in Lagos [29], Ota by Olukanni and Adebiyi, [41]. On the international level, the level observed in this study was lower than what was observed in Fallujah by Salah et al. [35], Palermo (Sicily), Italy by Manta et al. [68]. The concentration observed in this study was however higher than what was observed in Ghanzi-Kang and Tshabong-Sekoma, Botswana by Mmolawa et al. [52].

Manganese is an essential element in plant and animal nutrition [69], although it is toxic at high concentrations. Many foods in the human diet contain Mn, including spinach, tea, herbs, grains and rice, soya beans, eggs, nuts, olive oil, green beans and oysters. Harmful excessive manganese exposure in the workplace was recognised during the nineteenth century [70]. Manganese toxicity in humans mainly affects the respiratory tract and the brain; symptoms include hallucinations, forgetfulness and nerve damage. Manganese can also cause Parkinson's disease, lung embolism and bronchitis. An important significance of chronic manganism is its progressive development, even when exposure has cessed [71, 69, 72, 73]. Manganese deficiency, considered to be less than 0.11 mg Mn day^{-1} for adults, is more common than toxicity, and causes impaired reproduction and growth [25]. Symptoms of Mn deficiency include weight gain, glucose intolerance, blood clotting, skin problems, lowered cholesterol levels, skeleton disorders, birth defects and neurological symptoms.

IV. Conclusion

The data obtained in this study demonstrate that the heavy metal concentrations of urban soils can be used as powerful geochemical tracers for monitoring the impact of human activity, provided that background levels have been correctly interpreted and established. The results of this study indicates that, the levels of heavy metals (Pb, Cd, Cu, Cr, Zn and Mn) are mostly geogenic and that anthropogenic activities were additives. Analysis was done at the beginning and the end of the raining reason, during which the sky was cleaned of suspended particulate matter therefore there was less or no atmospheric deposition. The rainfall as at the period of sampling wasn't heavy enough that could cause leaching of the metals but flooding coupled with gravity of the rain and the physiochemical property of the soil might have contributed to the distribution pattern and observed levels of the metals within the Metropolis.

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Figure 1: The Yankari Motor Park

Figure 2: The Highway around Wunti market

Figure 3: Mechanical workshop along Jos Road Bauchi state

Figure 4: GRA residential Area, Bauchi Metropolis

Table I:

Concentration (ppm) of the Heavy Metals: Pb, Cd, Fe, Cu, Cr, Mn and Zn determined in the soil within Bauchi State Metropolis

Sites/ Elements	Pb	Cd	Fe	Cu	Cr	Mn	Zn
AMW	0.051[a] ±0.002	0.004 ±0.011	9.559[a] ±0.211	0.007 ±0.021	0.018[a] ±0.011	0.581 ±0.120	0.252 ±0.101
HW	0.006[a] ±0.001	0.002 ±0.001	10.630[a] ±0.231	ND	0.026 ±0.003	0.771 ±0.130	0.058 ±0.121
RA	0.005 ±0.003	ND	10.090[a] ±0.221	ND	0.016 ±0.121	0.980 ±0.121	0.053 ±0.002
BMP	ND	ND	10.121[a] ±0.121	ND	0.009[a] ±0.005	0.477 ±0.121	0.053 ±0.021

AMW= Automobile Maintenance Workshop, BMP= Car or motor parks, HW=Highways and RA= Residential Areas. Differences of the mean values with bold and same small letters within a column were found not significantly different at ($p \leq 0.05$) according to the Turkey test. Data are presented in mean ±SD (n = 4).