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GIS Mapping, Biomonitoring and Distribution of Heavy Metal Concentrations Using Neem (*Azadirachta indica*) Bark in Makurdi Town, Benue State, Nigeria

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Abstract

The present work determined the concentration and spatial distribution of heavy metals (As, Hg, Cr, Cd and Pb) in soil samples from Makurdi and its environs using geographic information system (GIS). The specific objective is to produce the spatial distribution maps showing the spatial distribution of toxic heavy metals in the study area. Inverse Distance Weighting (IDW), a GIS technique was used to produce dotted maps showing the spatial distribution of heavy metals in neem bark for better visualization of contamination zones and non-contamination zones. The map reveals few hotspot areas showing areas of high concentrations of the heavy metals investigated which were identified in red colours, the following concentration ranges were obtained; As (4.71 - 6.43 mg/kg), Cd (13.9 - 16.84 mg/kg), Cr (46.3 - 60.84 mg/kg), Hg (3.70 - 5.05 mg/kg) and Pb (24.02 - 31.34 mg/kg). These hotspot areas were found close to business outlets, fuel filling and service stations, farm sites where the application of fertilizers and pesticides were persistent coupled with heavy traffic of vehicles and other machinery which was associated with As, Hg, Cd, Pb and Cr been released into the environment thus, suggesting anthropogenic activities controlling the concentration of these heavy metals in the study areas. The cumulative effect of these heavy metals into the barks of neem could pose as danger, because this plant is used as herbs in folk medicine.

Keywords

Heavy Metal Contamination, Spatial Distribution, Inverse Distance Weighting, Folk Medicine, Makurdi

1. Introduction

Among many anthropogenic causes, rapid urbanization and industrialization are the two fundamental factors causing degradation of the environment. The world is turning towards an urbanized world and more than half of the population is living in urban areas. A variety of environmental problems have emerged, of which potentially toxic metals (PTMs) pollution is a major issue in urban and peri-urban areas (Altan et al., 2011). Heavy metals do not degrade, they undergo accumulation and bio-magnifications in the environment and are often regarded as chemical time-bombs. Once introduced into the environment, these metallic pollutants affect biological systems at various levels of enzyme systems through cells, organs, single organisms, population and the entire ecosystem. Therefore, monitoring of these metals in various matrices of the environment is important (Upasona et al., 2015).

Urban dust is often contaminated with hazardous substances which following dermal contact, ingestion or inhalation can cause cancer and non-cancer related adverse effects in humans and other organisms. Heavy metals in urban dust and soils are an important indicator of environmental contamination (Men et al., 2019). According to Sagar (2020), the atmospheric concentration and toxicity of urban dust depends on its location, nature of sources, proximity of sources, physico-chemical composition and season. Urban dust contains about 2 - 3 times the hazardous metal concentration found in urban soils.

Tree bark is one of the best bioindicators because it has high lipid content and large area and shows the amount of pollutants over a period of several years. The biomonitoring of tree bark is of significant interest because it is cheap, easy and there are many choices of tree species. Some characters of tree bark like its easy availability for sampling, present in large numbers, long living and easy identification makes it a candidate for an effective bio-monitor. Barks show high accumulation due to their perforations and so dust particles deposited in the attic duct of the bark can give precise information about changes that occur in an area (Abdullah et al., 2015).

In Makurdi, Benue State Nigeria, neem tree is a very common tree to see around, used as shade lining in most people's compounds and on the streets. Neem tree is a medicinal plant. In Nigeria, neem constitutes a vital role in human health due to the bark and leaves which are medicinal to people who believe in herbs (Bankole et al., 2018). Pure neem leaves and barks have found various applications locally in producing natural medicines and natural herbal cosmetics. Neem leaves are used to control high blood sugar level and is said to clean up the blood (Abdulateef et al., 2014). However, heavy metals accumulation in neem tree bark poses a serious threat to human health (Bankole et al., 2018). Up to now, several trees have been used for heavy metal monitoring. The most popularly used are neem, pine and moss. The suitability of neem tree as a bioindicator has been demonstrated in different studies (Lawal et al., 2011; Oklo & Asemave, 2012; Akan et al., 2012; Bankole et al., 2018). There is scarcity of such studies because no attempt has been made on the spatial distribution of As, Cd, Cr, Hg and Pb using geographic information system (GIS) to produce spatial distribution maps showing the spatial variation of these metals on tree barks in the study areas. However, GIS based mapping to show spatial variations of heavy metal concentration on tree barks in other parts of the world were undertaken by (Miri et al., 2017) in their studies on atmospheric heavy metals biomonitoring using a local *Pinus eldarica* tree and (Alexandrino et al., 2020) in biomonitoring of metal levels in urban areas with different vehicular traffic intensity by using *Araucaria heterophylla* needles.

The study is aimed at determining the concentration and spatial distribution of heavy metals (As, Hg, Cr, Cd and Pb) in neem bark samples from Makurdi and its environs using geographic information system (GIS). The specific objective is to produce the spatial distribution maps showing the spatial distribution of toxic heavy metals in the study area.

2. Study Area Description

The present study was conducted in Makurdi the capital of Benue State and the headquarters of Makurdi Local Government Area (LGA). The town is a rapidly growing city which lies between latitudes 7˚40'02''N and 7˚53'15''N and longitudes 8˚18'13''E and 8˚44'23''E in the Lower Benue River Basin, while, Abinsi, an outskirt town lies between latitudes 7˚36'04''N and 7˚53'17''N and longitudes 8˚44'23''E and 8˚44'24''E (**Figure 1**). Makurdi LGA has an approximate land mass of 804.35 km^2 and an estimated population of 517,342 persons including male and female as at 2017 (Shabu et al., 2021). The population in the city is unevenly distributed, land uses in the city include commercial, industrial, agricultural, residential housing, institutional, recreational and administrative, auto-mechanic workshops, transportation and uncultivated lands are scattered all over the city and these serve as point sources of heavy metals (Pam et al., 2013). Tree bark samples were collected from: Abinsi (Site AB), Agan (Site AG) villages, Ankpa Quarters (Site AQ), Apir (Site AP), Riverville Resort close to Benue State University, Zoological Garden (Control site BZ), (Bam Bam Community)-Makurdi Modern Market precinct (Site BB), Fiidi (Site FI), High Level (Site HL), Judges Quarters (Site JQ), Kanshio (Site KA), North Bank 1 (Site NB 1), North Bank 2 (Site NB 2), Old GRA (Lobi Quarters) (Site OG), Wadata (Agboughoul village) (Site AW), Wurukum (Akpehe) (Site WA) and Wurukum (Logo 1) (Site WL).

2.1. Materials and Methods

Sampling locations were chosen with the aim of covering the entire city so that

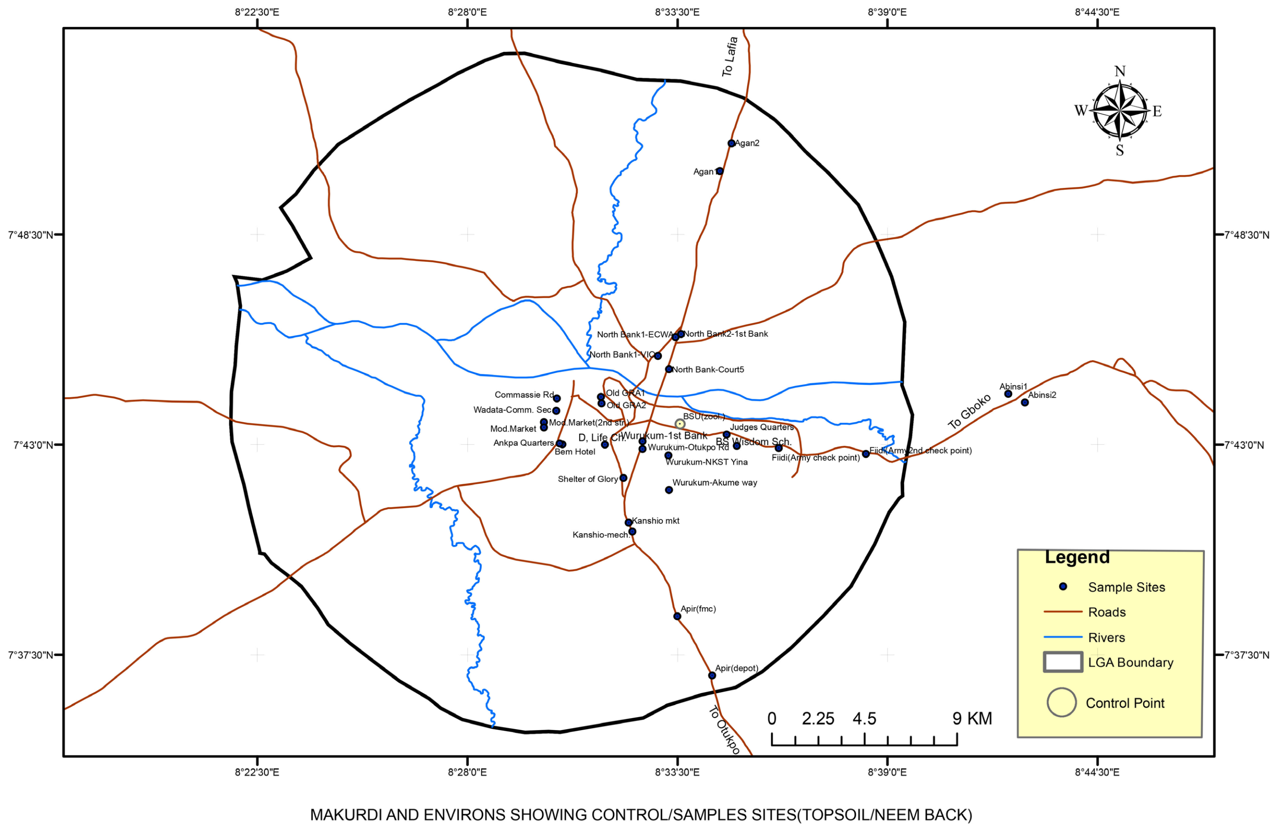

Figure 1. Map of Makurdi metropolis showing sample and control sites.

the number of samples would represent the different location types with different rates of land use activities. Random sampling of the neem (*Azadirachta indica*) barks were collected within Makurdi metropolis and its environs by cutting from the base of the tree with the aid of a pre-washed stainless matchet, manual debarking of the bark was done using a stainless-steel knife. The knife was washed after each sampling with 10% hydrogen trioxonitrate (V) acid to avoid cross contamination. The control sample was collected alongside from the Riverville Resort close to the Benue State University Zoological Garden. The bark samples collected were labeled accordingly and wrapped with papers, kept in a polythene bag and thereafter transported to the laboratory for further analysis (Ojekunle et al., 2014).

2.2. Digestion of Neem (*Azadirachta indica*) Bark Samples

The collected samples were dried in an oven at a temperature of 60˚C for 3 - 4 hours to a constant weight. Each neem bark samples were pulverized to uniform size for easy digestion with a mortar and pestle, which was thoroughly cleaned, and dried after each grinding to circumvent cross contamination. Two (2) gram of the powdered sample was weighed accurately into a pre-cleaned, vitreosil crucible, after which it was transported into a muffle furnace and preashed in the furnace, ashing was done for 15 minutes at a temperature of about 450˚C - 500˚C until the fumes vanished (Ojekunle et al., 2014). The cooled ashed sample was dissolved in 5.00 cm^3 of 11.6 M HCl solution, filtered, and then made up to 100 cm^3 in a volumetric flask using distilled water. The diluted sample was transferred to a pre-cleaned centrifuge tube for proper mixing and was centrifuged for 30 minutes at 3000 rpm speed. The supernatants were decanted into 100 cm^3 calibrated volumetric flasks, which was made up to the mark with the acid solution. Each digest was carried together with the blank in triplicates for the determination of As, Cd, Cr, Hg and Pb contents using Atomic Absorption Spectrophotometer.

Quality Assurance and Quality Control

Five working standards were prepared in triplicates for each metal by serial digestion of the stock solution prepared in 3:1. A procedural blank and a set of standards for each element were determined each time a series of samples were run. Average reading of the samples was corrected with the blank reading and a calibration curve was constructed for each standard solution (Ogundele et al., 2015). The concentrations of each element under investigation in mg/kg were determined from the curve of its standard by interpolation and analyzed using an Atomic Absorption Spectrophotometer, Phoenix 986 model at Golden Years Ltd, Port Harcourt, Nigeria.

2.3. Spatial Distribution Maps

The estimated maps of As, Cr, Cd, Hg and Pb were produced from the results obtained from the concentration of these metals after AAS analysis and the results were computed into Microsoft Excel application (Ver. 2007) where the data were converted to degrees and decimals with their respective coordinates transferred into the GIS environment in the ArcGIS 10.1 version (Ahmed et al., 2015). This method assumes that the variable being mapped decreases in influence with distance from its sampled location (Gisgeography, 2018).

The weights can be expressed as follows:

$$\widehat{v_1} = \sum_{i=1}^{n} \frac{1}{dp_i} v_i \bigg/ \sum_{i=1}^{n} \frac{1}{dp_i} \tag{1}$$

where, d_{p}, …, d_{pn} are the distance from the n data points to the power p of the point estimated. v_i is the known value and $\tilde{v}$ the value to be estimated.

The main factor affecting the accuracy of IDW is the value of the power parameter. The most popular choice of p is 2 and the resulting method is called inverse square distance (Fahad et al., 2016).

3. Result and Discussion

The heavy metal concentration in neem bark from fifteen sites in addition to the control site and their geographical coordinates are presented in **Table 1**.

Data were subjected to Statistical Package for Social Sciences (SPSS) 17.00 version and Microsoft excel 2007 windows such that descriptive statistics including mean, standard deviation and range were performed on the data, these were incorporated to represent the degree of dispersion distribution of different heavy metals and to indirectly indicate the activity of the selected elements in the studied sites as presented in **Table 2**.

Arsenic (As)

The level of As in neem bark was in a range of values from ND (Not Detected) across all the sites to 6.43 mg/kg at site NB1 (**Table 1**). The results obtained was lower than 0.05 - 1.18 mg/kg reported by (Yaghous et al., 2013) for studies of biomonitoring of airborne metals using tree leaves. However, the result was in a close range to 0.32 mg/kg reported by (Fosu-Mensah et al., 2017) and 4.52 mg/kg reported by (Ideisan & Zohuir, 2019). The presence of As at site NB1 may be attributed to moderate human/anthropogenic activities over the years.

Table 1. Heavy metals concentration in Neem bark and geographical coordinates of sampling site.

Sites/HMs	As	Cd	Cr	Hg	Pb	Latitude	longitude
AB	ND	2.07	13.30	ND	8.00	7˚47'28"N	8˚46'10E
AG	ND	0.80	12.20	ND	9.12	7˚46'26"N	8˚34'4"E
AQ	ND	2.33	16.60	ND	15.40	7˚43'17"N	8˚30'34"E
AP	ND	1.04	17.70	ND	15.39	7˚42'29"N	8˚32'19"E
BZ	ND	0.00	1.02	ND	1.70	7˚43'50"N	8˚33'24"E
BB	ND	2.10	17.70	ND	10.30	7˚43'31"N	8˚29'51"E
FI	ND	0.00	14.40	ND	6.30	7˚43'56"N	8˚32'20"E
HL	ND	2.10	18.00	ND	8.60	7˚42'08"N	8˚32'06"E
JQ	ND	0.00	15.50	ND	6.27	7˚43'15"N	8˚34'52"E
KA	ND	2.84	21.60	ND	16.00	7˚40'53"N	8˚32'20"E
NB1	6.43	13.90	60.70	5.05	31.40	7˚45'45"N	8˚32'06"E
NB2	ND	2.33	20.00	ND	12.00	7˚44'37"N	8˚33'11"E
OG	ND	0.00	13.30	ND	6.30	7˚44'21"N	8˚31'23"E
AW	ND	1.30	24.30	ND	10.33	7˚43'46"N	8˚30'44"E
WA	ND	16.84	25.50	ND	14.30	7˚44'29"N	8˚23'42"E
WL	0.00	2.03	23.24	ND	15.40	7˚71'80"N	8˚54'13"E

ND = Not Detected.

Table 2. Statistical summary of heavy metals concentration in Neem tree bark from Makurdi town and its environs.

Metals	Mean ± SD	Range
As	0.40 ± 1.61	6.43
Cd	2.98 ± 4.98	16.84
Cr	19.63 ± 12.43	59.84
Hg	0.32 ± 1.26	5.05
Pb	11.61 ± 6.70	29.70

Cadmium (Cd)

The level of Cd in neem bark was in a range of values from ND (Not Detected) to 16.84 mg/kg as shown in **Table 1**. Cd was not detected at sites HL, JQ, BB, OG and BZ (control), while the maximum concentration was detected at site WA. The level of Cd detected in this study was in a close range to that reported by (Yaghous et al., 2013) which is 2.8 to 15.84 mg/kg and below detection limit as reported by (Augustine et al., 2016). Similarly, the results were lower than 0.50 - 37.00 mg/kg reported by Bankole et al. (2018) for neem tree barks along major roads in Ibadan, Nigeria. However, the results were higher than that investigated by Abdulateef et al., (2014) which is 0.029 mg/kg and 0.11 mg/kg as reported by Ideisan & Zohuir (2019). The high levels of Cd may be as a result of prevailing human activities. Cd is extremely toxic to human, and in particular affects kidneys and bones causing severe bone disease (Wuana & Okieimen, 2011).

Chromium (Cr)

Table 1 shows that the values of Cr in the neem bark samples across the sites ranged between 1.02 mg/kg - 60.70 mg/kg and a mean value of 19.63 mg/kg. The higher concentration of Cr in the neem bark may be as a result of the different kinds of Cr that differ in their effects and upon the route which they enter air, water and the soil. Cr^{3+} and Cr^{6+} form through natural processes and human activities (Ogundele et al., 2015). The results obtained for Cr in neem tree bark was higher than 0.028 mg/kg reported by (Abdulateef et al., 2014), 0.22 - 0.38 mg/kg reported by (Erakhrumen & Inaede, 2018) and 0.81 mg/kg reported by Ideisan & Zohuir (2019).

Mercury (Hg)

The level of Hg concentration in neem bark was not detected across all the sites, however the highest concentration was observed at site NB1 having a concentration value of 5.05 mg/kg. The results obtained for Hg in neem bark was lower than 2.49 - 4.03 mg/kg reported by (Fosu-Mensah et al., 2018) and 8.6 - 41.0 mg /kg reported by Olatunde & Onisoya (2017). This low value may be as result of moderate human activities at site NB1. Plants growing close to the roads are being contaminated with these HMs as a result of exposure thereby contributing to environmental cleaning. Trees play a vital role in controlling heavy metal pollution in an area and in soil of tree planted in these areas through mechanism known as phytoremediation (Erakhrumen & Inaede, 2018). Phytoremediation is one of the functions performed by neem tree from which barks were obtained for experiment in this research. However, the possibility for other sources of contaminants such as application of fertilizers to soil, auto electrical repairs, use of leaded paints in artisan workshop, waste disposal, welding, vulcanizing, battery charging and dealing with other transportation facilities contributes a lot to pollution (Dizaji et al., 2016).

Lead (Pb)

The level of Pb in the neem bark varied widely from 1.70 mg/kg to 31.40 mg/kg across all the sites, while NB1 had the highest concentration of 31.40 mg/kg (**Table 1**). The concentrations of Pb were moderately high across all the sites for the neem bark samples, these high values could probably be attributed to persistent anthropogenic activities like high vehicular movements, effluents from storage batteries which contain Pb and this could influence the deposition of lead in the soil in these sites which could trigger emission of fumes/smoke containing Pb (Lawal et al., 2011). The lower concentrations of Pb in the neem bark samples from other sites could be attributed to low automobile and commercial activities in the areas. Elevated levels of lead constitute serious health risk which is known for lead poisoning in humans as well as chronic neurological disorders especially in fetuses and children (Opaluwa et al., 2012). According to Phuntsog et al. (2017) lead (Pb) impedes the synthesis of hemoglobin and accumulates within the red cells as well as the bones to give rise to anemia, headache and dizziness. The results obtained were lower than that investigated by Bankole et al. (2018) which was 66.50 mg/kg and 85.56 mg/kg as reported by Fosu-Mensah et al. (2018). However, the result was higher than 0.45 - 3.05 mg/kg reported by Yaghous et al. (2013) for biomonitoring of airborne metals using tree leaves.

4. Spatial Distribution Maps of Heavy Metals

The maps obtained were dotted maps which shows the spatial distribution and concentration of these metals across the investigated sites as presented in **Figures 2-6**.

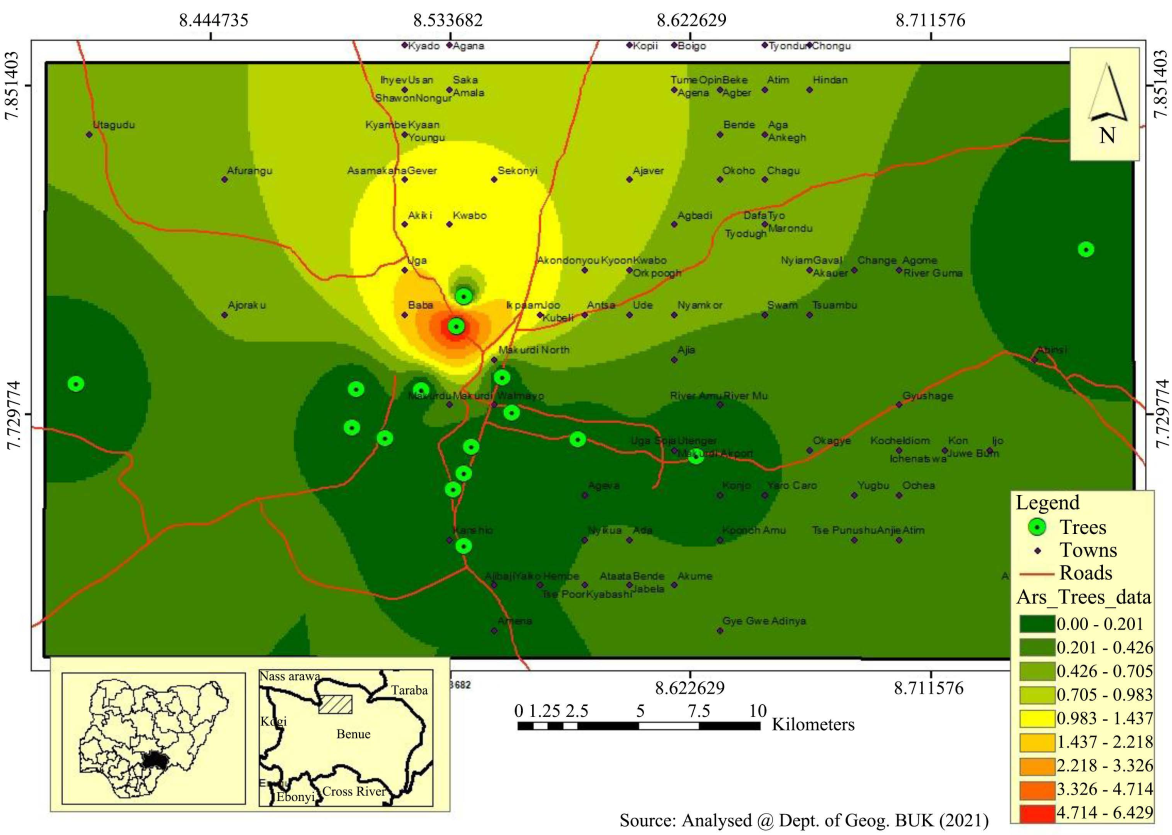

Figure 2. Spatial distribution of As in Neem bark from the study areas.

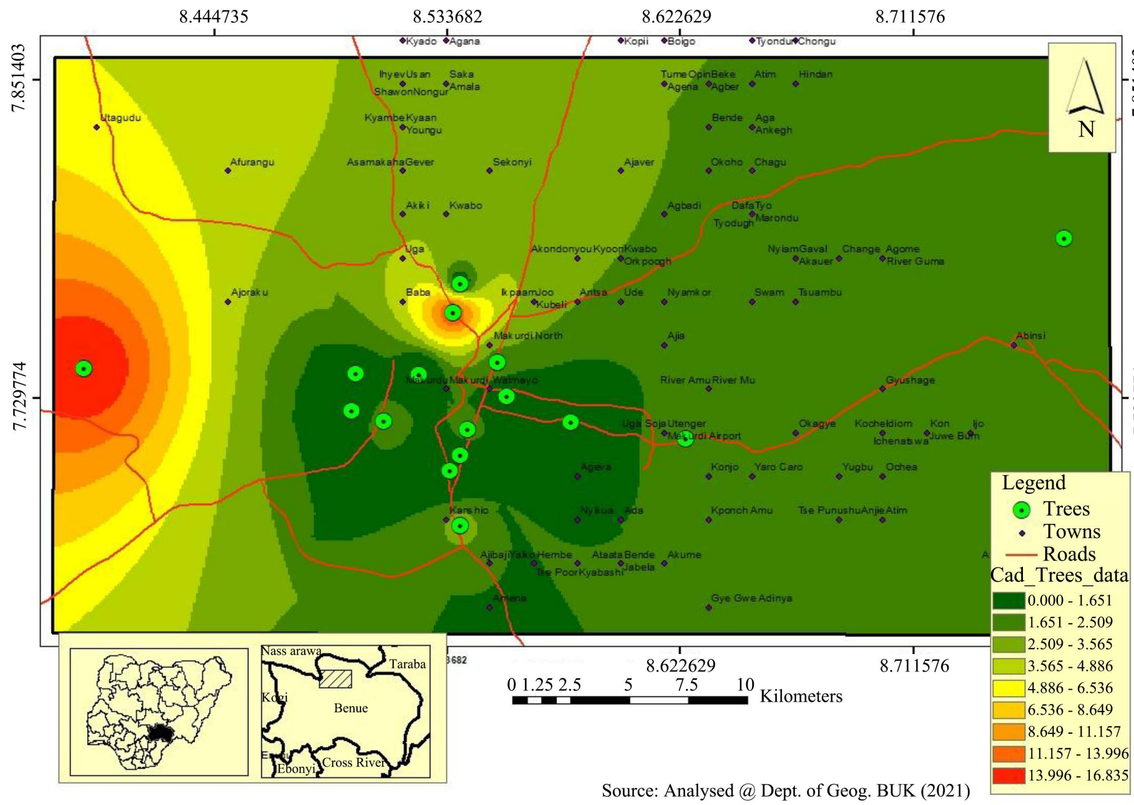

Figure 3. Spatial distribution of Cd in Neem bark from the study areas.

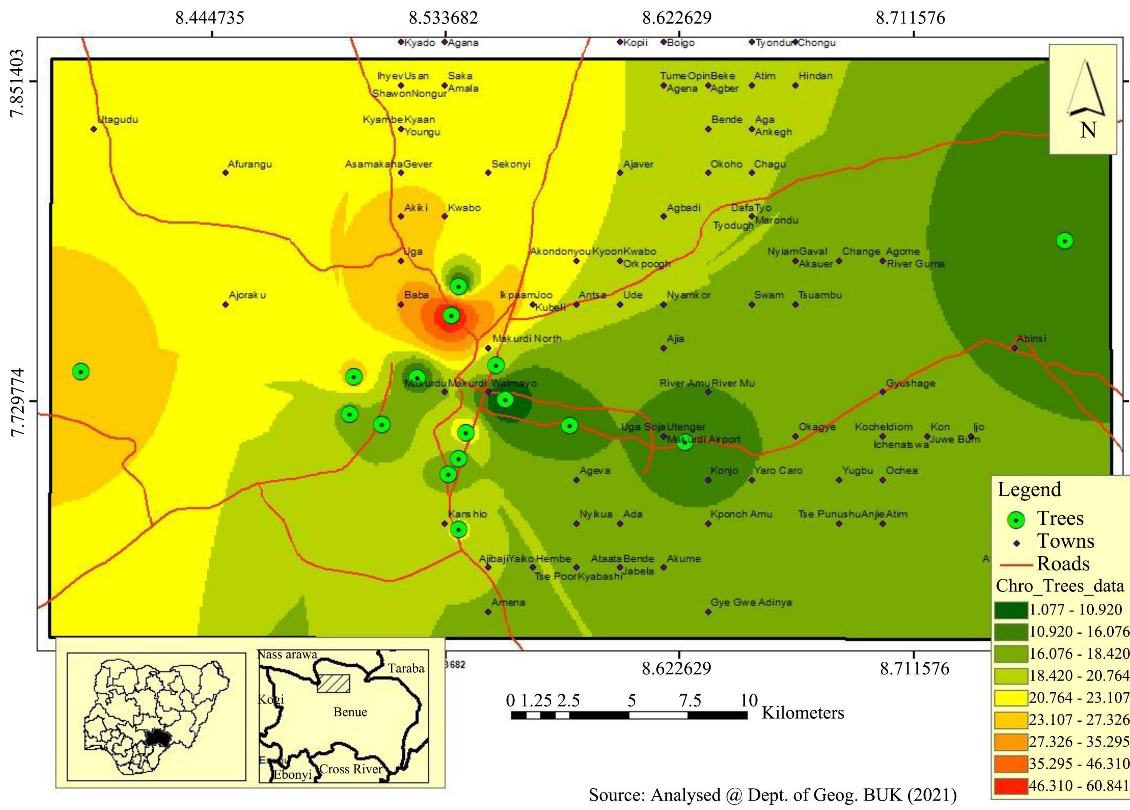

Figure 4. Spatial distribution of Cr in Neem bark from the study areas.

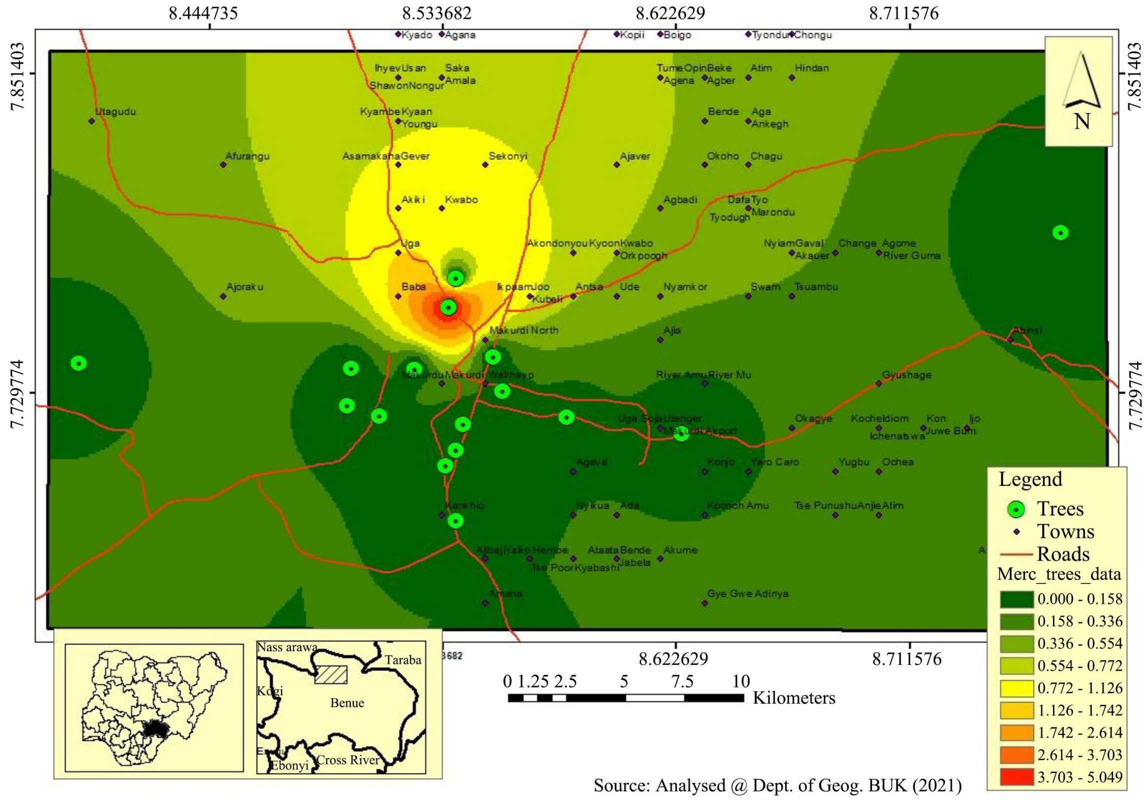

Figure 5. Spatial distribution of Hg in Neem bark from the study areas.

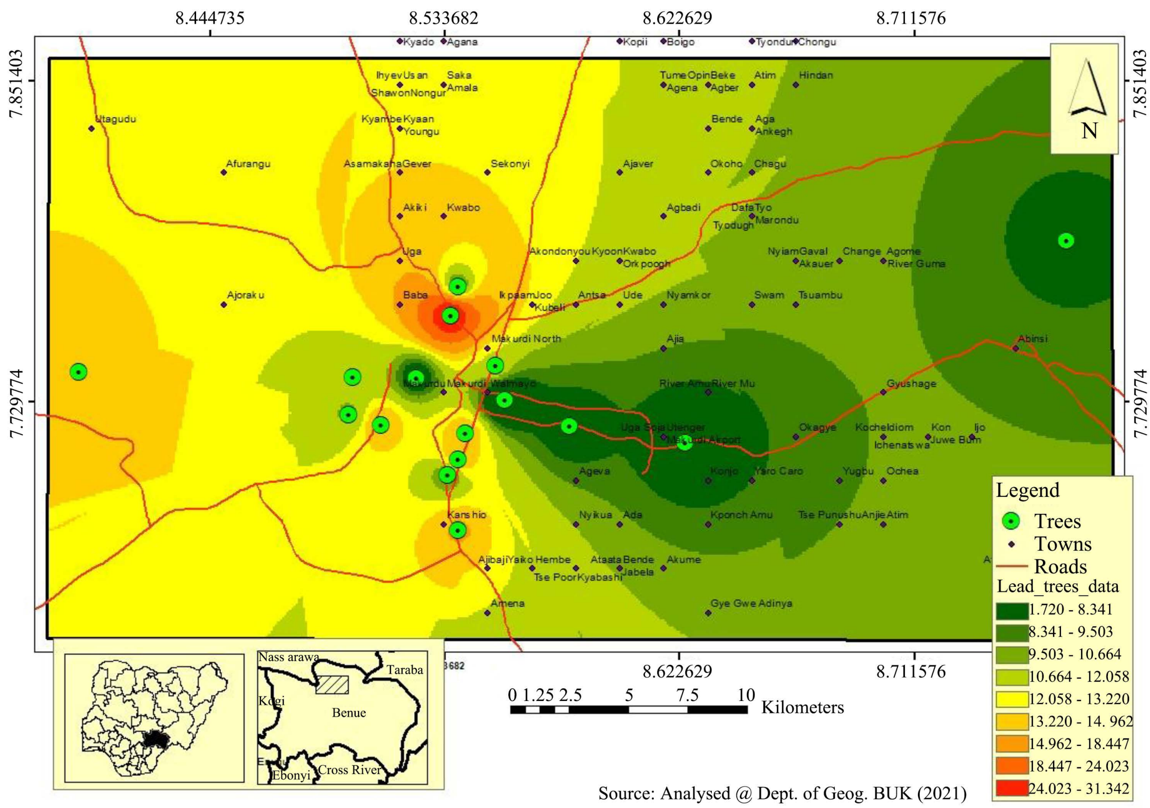

Figure 6. Spatial distribution of Pb in Neem bark from the study areas.

The map shown in **Figure 2**, shows only one hotspot area with a red colour (located at the northern region of the study area) which falls within the concentration range of 4.714 mg/kg - 6.429 mg/kg signifying a high spatial distribution of As. This study is similar to studies reported by Yaghous et al. (2013) in their assessment of airborne metals using tree leaves. The high value may be as a result of proximity of the site to anthropogenic activities (heavy vehicular movement, the use of generators and lubricating oils by business outlets).

Figure 3, shows two (2) hotspots areas indicated with red colour showing the areas where the concentration of Cd is high (observed at the western and northern part of the area under study) with a concentration range of values between 13.996 mg/kg - 16.835 mg/kg. The high value of Cd may be as a result of proximity of the site to anthropogenic activities. **Figure 4**, shows that there is only one (1) spot with a brown colour at the western part of the study area which shows that the concentration level of Cr is moderately high with concentration range of values ranging between 27.328 mg/kg - 35.298 mg/kg. However, the only hotspot area with a red colour is located at the northern part of the study area with a concentration range of values between 46.310 mg/kg - 60.841 mg/kg. This study is similar to studies carried out by Alexandrino et al. (2020) in their study of biomonitoring of HMs using *Araucaria heterophylla*, these values may be due to the prevailing human activities.

Figure 5 shows that Hg was not spatially distributed as shown in the estimated map across all the sites, the red colour at the northern part of the map indicates a hotspot area where elevated concentration of Hg was observed with concentration range between 3.703 mg/kg - 5.049 mg/kg. The spatial distribution map of Pb as shown in **Figure 6** shows five (5) spots with dark brown colour where the concentration levels was found to be relatively high at the western, southern and northern part of the map with concentration values between 14.962 mg/kg - 16.447 mg/kg. However, the only spot with a red colour at the northern part of the study area indicates a hotspot area having a concentration range of value between 24.023 mg/kg - 31.342 mg/kg. This study is similar to studies reported by Yaghous et al. (2013). The high concentrations of Pb could be attributed to the proximity of the areas and the prevailing human activities such as the continuous use of pesticides and fertilizers in agriculture, exhaust gases from cars, activities of fuel filling and service stations, effluents from storage batteries in the location which contain Pb and this could trigger emission of fumes/smoke containing Pb.

5. Conclusion

The results of this study have indicated the suitability of *Neem Azadirachta indica* bark as potential bioindicator for As, Cd, Cr, Hg and Pb from various sites in Makurdi metropolis, Benue State. This might be attributed to the geological status of the areas under investigation, the deviation in metal concentrations amongst the studied sites could be due various anthropogenic activities as result of different land use. The Geographic information systems (GIS)—based mapping technique applied in this study to predict the spatial distribution of metals across the study area showed a few hotspot areas of elevated concentrations of As, Cd, Cr, Hg and Pb shaded in red colour which were indicated over the study areas. These points were found to be close to the roadside which was associated with As, Hg, Cd, Pb and Cr released into the environment compared to the residential and agricultural sites. The green spot areas on the map indicate a low concentration level of contamination of the metals investigated. Therefore, this study provides useful information on urban environmental monitoring. This study further confirms the increased danger of environmental pollution. As a result, these metals can pose a risk to human health due to continuous consumption. It is advisable that people living along this highway should desist from using the barks of this tree for herbal purposes. Further monitoring of plant barks as well as lower and higher epiphytes and vascular plants is needed in order to determine whether any temporal trend exist in metal concentration among biological indicators.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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