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Ecological Risk Assessment of Heavy Metals Concentrations in Topsoil of Makurdi and Its Environs

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Abstract

This work examined the concentrations of As, Cd, Cr, Hg and Pb pollution in soil and estimated the potential ecological risks of these metals in Makurdi and its environs, using established pollution indices. The information derived from pollution indices will help to assess the extent, and intensity of anthropogenic contaminant deposition on surface soil in the study area. The soil samples were collected from sixteen (16) locations across the investigated sites, sampled as appropriate and treated using established methods and analyzed using atomic absorption spectrometry (AAS). The findings have revealed that the concentrations of the metals in the topsoil samples were arranged in the sequence from increasing to decreasing order thus: Cr > Pb > Cd > Hg > As. It was observed that the pollution levels of As and Hg were insignificant, while, the level of pollution caused by Cd, Cr and Pb ranged from low level of contamination to high level of contamination across the investigated sites, except, for the control site (BZ) whose pollution level was insignificant with respect to the heavy metals studied. The results could be used as preliminary baseline data for heavy metal concentrations for future assessment and monitoring. Therefore, there is an urgent need to effect mitigation measures to reduce the ecological environmental risks, taking into consideration that human activities which are the main source of pollutants are still ongoing in the study area.

Keywords

Pollution, Contamination, Single Indices, Integrated Indices, Makurdi

1. Introduction

The term heavy metal chiefly arose with discussions of pollutants discharged to

the environment in the form of air, water or soil contaminants. While many heavy metals have considerable toxicity, others are deemed not to possess significant toxic properties, and, in fact, several of these elements including zinc, iron, copper, chromium and cobalt are necessary for metabolic function for a large class of organisms. Although some heavy metals are essential micronutrients for animals, plants and many micro-organisms, depending on the route and dose, all heavy metals demonstrate toxic effects on living organisms via metabolic interference and mutagenesis. Animal health impacts range from reduction in fitness, to reproductive interference to carcinoma, with many exposures being lethal (Augustine et al., 2016). More systematically, these are metals or metalloids with density less than or equal to 5.0 g/cm^3.

The environmental problem with heavy metals is that they are unaffected during breakdown of organic waste and have toxic effects on living organisms when they exceed a certain concentration. The high concentration of heavy metals in soils is reflected by their concentrations in plants, water, animal, and human bodies (Oladunni et al., 2012).

There are two different sources for heavy metals in the environment. These sources can be both of natural or anthropogenic origin. There are a multitude of anthropogenic emissions in the environment. Heavy metals enter into the environment mainly via three routes: 1) Deposition of atmospheric particulates (mining, smelting, fossil fuel combustion, municipal waste incineration, cement production and phosphate mining). 2) Disposal of metal enriched sewage sludge and sewage effluents, commercial fertilizers and pesticides and animal waste especially to the terrestrial and aquatic environment. 3) By-products from metal mining processes. The sources of heavy metal emissions from vehicles include fuel combustion, lubricating oil consumption, tire wear, brake wear, road abrasion, etc. Cd emission is mainly from lubricating oil consumption and tire wear. Brake wear is the most important source for Cu and Pb emissions. Lead comes also from exhaust gas and worn metal alloys in the engine. Through the atmospheric deposit or road runoff, heavy metals can be transported into the roadside soils, where tree barks absorb these heavy metal elements from the soils through their roots (Xuedong et al., 2012).

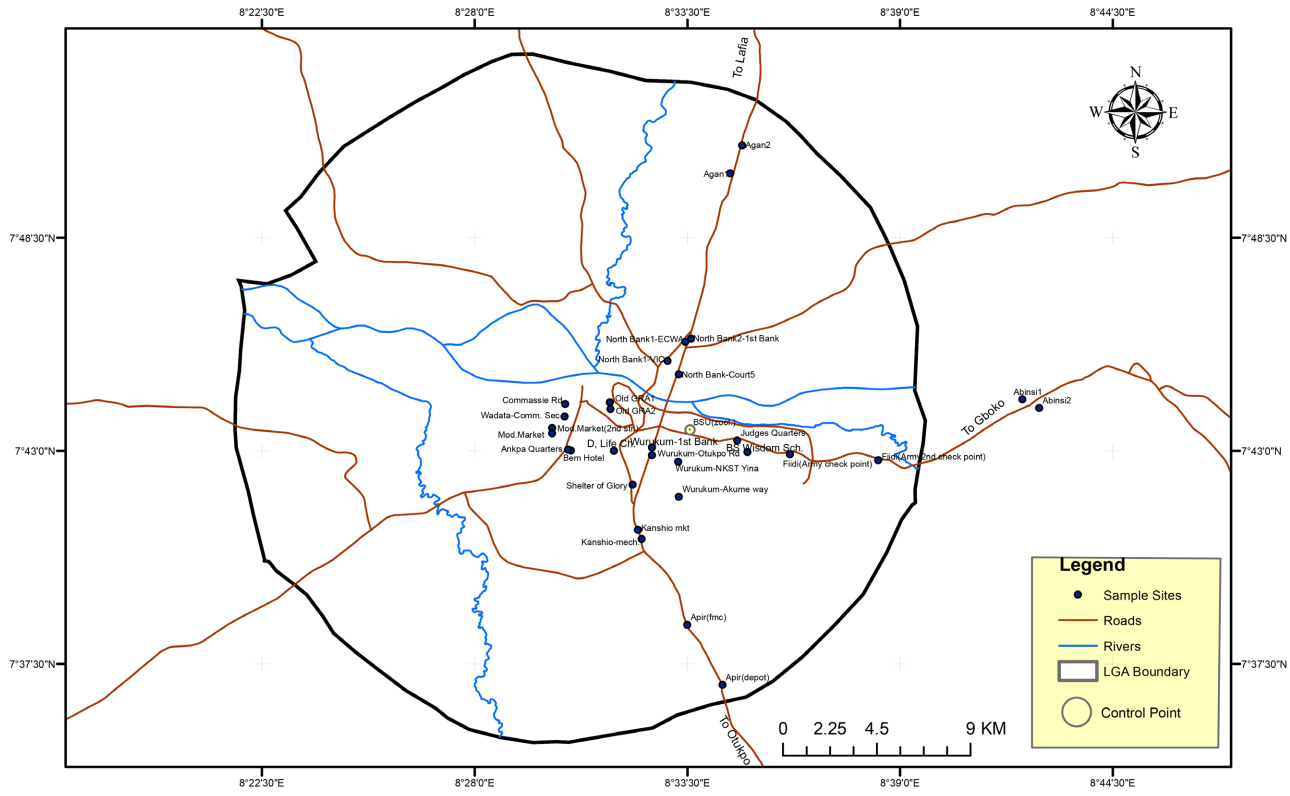
Soil is the major reservoir for contaminants and has an ability to bind various chemicals. These chemicals can exist in various forms in the soil and different forces keep them bound to soil particles. Diverse amounts of heavy metals may be found everywhere in the soils (Salisu et al., 2016). Soil is considered to be useful in atmospheric pollution studies due to the low cost, simplicity of analytical procedures, and ease of chemical analysis. Numerous studies have shown that soils obtain a large input of trace metals from different anthropogenic sources, especially from industrial areas and vehicle emissions. Sedimentation, impaction and interception processes from the deposition of particles on all environmental surfaces cause soils to act as a sink for the metallic load (Mohd Zahari & Abdulkadir, 2015). Therefore, the environmental problem of soil and sediment pollution by heavy metals has received increasing attention in the last

few years in both developed and developing countries throughout the world (Lodhaya et al., 2017).

The current study examines the concentration levels of As, Cd, Cr, Hg and Pb pollution in soil and to estimate the potential ecological risks of these metals in Makurdi and its Environs using pollution indices. The information derived from pollution indices will help to assess the extent, degree of metals and the intensity of anthropogenic contaminant deposition on surface soil.

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" and 7˚53'15"N and longitudes 8˚18'13" and 8˚44'23"E in the Lower Benue River Basin, while, Abinsi, an outskirt town lies between latitudes 7˚36'04" and 7˚53'17"N and longitudes 8˚44'23" 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 lands, residential housing, institutional, recreational and administrative, auto-mechanic workshops, transportation and uncultivated lands are scattered all over the city and



MAKURDI AND ENVIRONS SHOWING CONTROL/SAMPLES SITES(TOPSOIL/NEEM BACK)

Figure 1. Map of Makurdi and its environs showing the control and sample sites.

these serve as point sources of heavy metals (Pam et al., 2013). Soil 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. Sampling of Soil Samples and Preparations

Soil samples were collected by random sampling from a depth of 0 - 15 cm (top soil) (**Figure 1**) using a stainless-steel hand trowel and packaged in clean labeled polythene bags, Care was taken to wash and clean the hand trowel before sampling each location in order not to contaminate the samples, the samples were transported to the laboratory and sun dried for about five days. The dried samples were later disintegrated using a mortar and pestle and further sieved using −80 mesh nylon sieve (Sikakwe, 2018).

2.2. Soil Sample Digestion

All the reagents used were of analytical grade. Wet digestion method was used in which 1 g of each air-dried powdered soil sample were weighed accurately and transferred into a 250 cm^3 digestion flask. a mixture of 10 cm^3 concentrated hydrochloric acid (HCl) and 3.5 cm^3 concentrated nitric acid (HNO_3), was added to the samples and the digestion flask heated on a hotplate in a fume hood until a white fume was observed which signified that digestion was completed. Twenty (20) cm^3 of distilled water was then added to the digest after cooling to room temperature. The digest were filtered using Whatman filter paper into a 100cm^3 volumetric flask and made up to the 100 cm^3 mark with distilled water. The solutions were transferred into sampling bottles for analysis. The concentration of these heavy metals in the samples was analyzed using an Atomic Absorption Spectrophotometer, Phoenix 986 model at Golden Years Laboratory, Port Harcourt, Nigeria.

2.3. Quality Assurance and Control

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 which was linear within the concentration range. The concentrations of each element under investigation in mg/kg were determined from the curve of its standard by interpolation (Ogundele et al., 2015; Abdulrashid et al., 2017).

3. Pollution Indices Used for Assessment of Metal Contamination

Pollution assessment models are indicators used to assess the presence and in-

tensity of anthropogenic contaminant deposition on soils. Pollution indices help in assessing the metal contamination. Pollution indices of heavy metal contamination can be classified as single pollution indices and integrated pollution indices. Single indices are indicators used to calculate only one metal contamination, which include contamination factor, enrichment factor and index of geo-accumulation (Gong et al., 2008; Lodhaya et al., 2017). Integrated indices are indicators used to calculate more than one metal contamination, which were based on the single indices. Each kind of integrated index might be composed by single indices separately (Gong et al., 2008).

3.1. Single Indices

1) Contamination factor

Contamination Factor is described as the level of contamination of soil by metal. Contamination factor (Cf) is ratio of the concentration of the element in samples to pre-industrial reference value for the element. It is expressed as follows using Equation (1):

$$c_f^i = \frac{C_e}{C_{pi}} \tag{1}$$

where, C_e the concentration of the element in samples and C_{pi} is the concentration of the pre-industrial reference value for the element (Hakanson, 1980). The different contamination factor levels are shown in Table 1.

2) Index of geo-accumulation

An index of geo-accumulation (Igeo) was originally defined by Müller in 1969, in order to determine and define metal contamination in sediments by comparing current concentrations with pre-industrial levels. It can be calculated by using the following Equation (2):

$$\text{Igeo} = \log_2 \frac{C_1}{1.5C_{ri}} \tag{2}$$

where C_i is the measured concentration of the examined metal i in the sediment, and C_{ri} is the geochemical background concentration or reference value of the metal i. Factor 1.5 is used because of possible variations in background values for a given metal in the environment as well as very small anthropogenic influences (Muller, 1969; Gong et al., 2008; Lodhaya et al., 2017). Table 2 shows seven (7) different classes of index of geo-accumulation values.

3) Enrichment factor (EF)

It is an indicator used to assess the presence and intensity of anthropogenic

Table 1. Terminologies used to describe the different contamination factor level in soil.

Contamination factor (Cf)	Contamination level
Cf < 1	Low contamination
1 < Cf < 3	Moderate contamination
3 < Cf < 6	Considerable contamination
Cf > 6	Very high contamination

Table 2. Different classes of index of geo-accumulation values.

Class	Igeo values	Sediment quality
0	Igeo ≤ 0	Uncontaminated
1	0 < Igeo < 1	Uncontaminated to moderately Contaminated
3	2 < Igeo < 3	Moderately to heavily Contaminated
4	3 < Igeo < 4	Heavily contaminated
5	4 < Igeo < 5	Heavily to extreme contaminated
6	Igeo > 5	Extremely contaminated

contaminant deposition on surface soil. These indexes of potential contamination are calculated by the normalization of one metal concentration in the topsoil respect to the concentration of a reference element. A reference element is an element particularly stable in the soil, which is characterized by absence of vertical mobility and/or degradation phenomena. Aluminum is a conservative element and a major constituent of clay minerals and has been used successfully by many scientists (Lodhaya et al., 2017). The Enrichment factor can be calculated with the formula derived from Equation (3):

$$\mathrm{EF} = \frac{\left(C_i / C_{ie}\right)_s}{\left(C_i / C_{ie}\right)_{RS}} \tag{3}$$

where, C_i is the content of element i in the sample of interest or the selected reference sample, and C_{ie} is content of immobile element in the sample or the selected reference sample. $(C_i/C_{ie})_S$ is the heavy metal to immobile element ratio in the samples of interest, and $(C_i/C_{ie})_{RS}$ is the heavy metal to immobile element ratio in the selected reference sample (Gong et al., 2008). Five enrichment factor categories are recognized based on enrichment factor values and these categories are shown in **Table 3**.

3.2. Integrated Indices

1) Pollution load index (PLI)

The Pollution load index (PLI) represents the number of times by which the heavy metal concentrations in the sediment exceeded the background concentration and give a summative indication of the overall level of heavy metal toxicity in a particular sample and is determined as the nth root of the product of nCF. It was developed by Tomlinson et al. (1980). It is calculated using the Equation (4):

$$\mathrm{PLI} = \left(\mathrm{CF}_1 \times \mathrm{CF}_2 \times \mathrm{CF}_3 \times \cdots \times \mathrm{CF}_n\right)^{1/n} \tag{4}$$

where n is the number of metal and CF_n is the contamination factor value of metal n analyzed. The pollution index levels are categorized in three levels (Jiang et al., 2017; Wuana et al., 2019). The pollution load index is categorized into three (3) different classes as seen in **Table 4**.

2) Modified degree of contamination (mCd)

The modified degree of contamination was introduced to estimate the overall

Table 3. Different categories of EF values which describes the enrichment of the element in the soil.

EF values	EF categories
EF < 2	Deficiency to minimal enrichment
2 < EF > 5	Moderate enrichment
5 < EF > 20	Significant enrichment
20 < EF > 40	Very high enrichment
EF < 40	Extremely high enrichment

Table 4. Terminologies used to categorize different grades of PLI and RI.

Pollution load index category	Soil quality	Grades of overall risk of contamination
PLI < 1	Perfect	Low soil quality
PLI = 1	Only baseline levels of	Moderate soil quality
	Pollutants are present	Considerable soil quality
PLI > 1	Deterioration of soil quality	Very high soil quality

degree of contamination at a given site. It is a modified equation for calculating contamination factor according to the formula:

$$\mathrm{mCd} = \sum_{i=1/n}^{i=n} \mathrm{CF} \tag{5}$$

where n-number of analyzed elements and i is the ith element (or pollutant) and CF is contamination factor. The modified formula is generalized as follows: a) by defining the degree of contamination (mCd) as the sum of all the contamination factors (CF) for a given set of sediment pollutants divided by the number of analyzed pollutants, b) the mean concentration of a pollutant element is based on the analysis of at least three samples and c) The baseline concentrations are determined from standard earth materials (Lodhaya et al., 2017). Using this generalized formula to calculate the mCd allows the incorporation of as many metals as the study may analyse with no upper limit (Sivakumar et al., 2016). The description and different degree levels for modified contamination degree are shown in Table 5.

3) Nemerow pollution index (P_{nemerow})

It is usually applied to assess the quality of soil environment widely and is expressed as:

$$P_{\text{nemerow}} = \sqrt{\left[\left(1/m\sum_{i=1}^{m} P_i\right)^2 + \left(P_{\max}\right)^2\right]\Big/2} \tag{6}$$

where, P_i is the single pollution index of heavy metal i; $P_{\max}$ is the maximum value of the single pollution indices of all heavy metals, and m is the number of the heavy metal species (Nemerow, 1985). The nemerow pollution index is categorized into five (5) different classes as seen in Table 6.

4) Contamination degree (Cdeg):

Hakanson proposed contamination degree as a measure of the overall contamination in surface layers of soil at respective sites. Contamination degree is

Table 5. Terminologies used to describe modified contamination degree values (mCd).

Modified contamination degree mCd	Modified degree of contamination
mCd < 1.5	Nil to very low degree of contamination
1.5 ≤ mCd < 2	Low degree of contamination
2 ≤ mCd < 4	Moderate degree of contamination
4 ≤ mC < 8	High degree of contamination
8 ≤ mCd < 16	Very high degree of contamination
16 ≤ mCd < 32	Extremely high degree of contamination
mCd ≥ 32	Ultra high degree of contamination

Table 6. Terminologies used to understand different grades of Nemerow pollution index.

Grades of Nemerow pollution index	Terminologies used for Pollution Grade
$P_{\text{nemerow}} \leq 0.7$	Clean
$0.7 < P_{\text{nemerow}} \leq 1$	Warning limit
$1 < P_{\text{nemerow}} \leq 2$	Slight pollution
$2 < P_{\text{nemerow}} \leq 3$	Moderate pollution
$P_{\text{nemerow}} > 3$	High pollution

the sum of contamination factor of all elements (Hakanson, 1980), it is expressed in Equation (7) as:

$$\text{Cdeg} = \sum_{i=1}^{n} \text{Cf} \tag{7}$$

4. Results

Heavy metals concentrations in top soil samples from sixteen (16) sites for all the elements investigated are shown in Table 7.

The contamination factor, pollution load index, the degree of contamination, the modified degree of contamination and nemerow pollution index of the selected heavy metals in top soil under different land uses in Makurdi and its environs and their respective classification are presented in Table 8.

The index of geo-accumulation of the selected heavy metals under different land uses in Makurdi and its environs are presented in Table 9.

5. Discussions

Heavy metals concentration

The concentration of soil samples under study were run on AAS in duplicates for all the elements under study as shown in Table 7. These values were used to evaluate the pollution indices further.

As concentrations recorded in the soil samples ranged from ND to 6.30 mg/kg. The results were lower than 12.49 - 173.2 ppm reported by (Tsuwang et al., 2014) in soils of Anka, Nigeria. However, the results were higher than 0.06 mg/kg reported by (Opaluwa et al., 2012) and 1.00 - 2.06 mg/kg reported by (Fosu-Mensah et al., 2017). This is an indication of low contamination from anthropogenic factors. The presence of As in some of the sites may be attributed

to moderate human/anthropogenic activities. The magnitude of As concentration in the top soil samples follows the sequence from highest to lowest as WL >

Table 7. Heavy metals concentrations in top soil in Makurdi town and its environs.

Sites/ HMs Parameters	As	Cd	Cr	Hg	Pb
AB	4.24	8.30	36.52	0.90	17.67
AG	ND	8.03	26.7	0.91	17.70
AQ	ND	5.90	36.52	ND	13.11
AP	4.90	10.62	51.00	3.73	23.40
BZ (control)	ND	2.33	20.34	ND	12.00
BB	ND	5.70	38.73	ND	19.40
FI	ND	8.03	45.40	ND	17.70
HL	4.10	15.02	58.70	2.32	27.40
JQ	ND	7.51	32.10	ND	16.50
KA	5.90	12.43	49.80	5.10	27.40
NB1	ND	11.40	47.60	2.32	22.00
NB2	4.06	12.70	48.70	4.12	26.80
OG	0.92	5.70	35.41	ND	12.54
AW	5.17	13.73	67.50	5.90	30.21
WA	4.43	15.80	67.50	ND	29.10
WL	6.30	16.80	56.43	8.73	30.21

Table 8. Contamination factor (Cf), pollution load index (PLI), degree of contamination (Cdeg), modified degree of contamination and Nemerow pollution index of top soil samples across the studied sites.

SITES/	Contamination Factor (Cf)					Degree of contamination (Cdeg)		Pollution Load index	Nemerow Pollution indices
HMs	As	Cd	Cr	Hg	Pb		Mean	(PLI)	($P_{nemerow}$)
AB	0.00	3.60	1.80	0.00	1.50	6.90	1.38	1.60	2.80
AG	0.00	3.50	1.31	0.00	1.50	6.30	1.26	1.47	2.70
AQ	0.00	2.60	1.80	0.00	1.10	5.50	1.10	1.40	2.00
AP	0.00	4.60	2.51	0.00	1.92	9.03	1.81	1.17	3.52
BZ	0.00	1.00	1.00	0.00	1.00	3.00	0.60	1.00	0.70
BB	0.00	2.50	1.90	0.00	1.62	6.02	1.20	1.43	1.90
FI	0.00	3.52	2.20	0.00	1.50	7.30	1.46	1.63	1.90
HL	0.00	6.52	2.90	0.00	2.30	11.70	2.34	2.13	2.71
JQ	0.00	3.26	1.60	0.00	1.38	6.24	1.25	1.48	2.50
KA	0.00	5.40	2.45	0.00	2.30	10.20	2.04	1.90	4.10
NB1	0.00	4.90	3.00	0.00	1.83	9.73	1.94	1.93	3.73
NB2	0.00	3.60	2.40	0.00	2.30	8.30	1.66	1.82	2.81
OG	0.00	2.48	1.74	0.00	1.04	5.28	1.06	1.40	1.93
AW	0.00	5.90	3.30	0.00	2.50	11.0	2.20	2.18	4.50
WA	0.00	6.90	3.30	0.00	2.43	12.63	2.52	2.23	5.20
WL	0.00	7.30	2.80	0.00	2.50	12.60	2.52	2.19	5.47
			Total				132.43	26.90	NA
			mCd (mean)				26.50	NA	NA

Table 9. Index of geo-accumulation and enrichment factor of soil samples collected across the studied sites.

SITES/ HMs	AB	AG	AQ	AP	BZ	BB	FI	HL	JQ	KA	NB1	NB2	OG	AW	WA	WL
Geoaccumulation index																
As	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cd	0.76	0.74	0.46	0.90	0.00	0.42	0.74	1.30	0.66	1.10	0.71	0.76	0.42	1.19	1.31	1.36
Cr	0.15	1.17	0.15	0.45	−0.35	0.21	0.35	0.60	0.04	0.42	0.60	0.41	0.13	0.69	0.69	0.53
Hg	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Pb	−0.09	−0.09	−0.27	0.23	−0.36	0.83	−0.09	0.37	−0.07	0.37	0.17	0.35	−0.32	0.46	0.42	−0.46
Mean	0.16	−0.104	0.07	0.33	−0.14	0.29	0.20	0.45	0.13	0.34	0.29	0.30	0.05	0.47	0.48	0.29
Enrichment factor																
As	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cd	3.60	3.50	2.60	4.61	1.00	2.50	3.50	6.52	3.50	5.40	4.90	3.60	2.50	6.00	6.90	7.40
Cr	1.80	1.31	1.80	2.51	1.00	1.92	2.23	2.90	1.60	2.60	3.00	2.41	1.74	3.33	3.33	2.80
Hg	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Pb	1.32	1.52	1.10	1.90	1.01	1.63	1.52	2.30	1.40	2.31	1.83	2.30	1.05	2.54	2.44	2.54
Mean	5.70	5.10	4.60	7.49	2.20	4.72	6.03	9.80	5.40	8.46	8.30	6.50	4.50	9.80	10.68	10.71

KA > AW >AP > WA > AB > NB2 > HL > OG > AG > AQ. > BB > BZ > FI > JQ > NB1.

Cd concentration in the soil samples from various sites were in a range of 2.33 mg/kg to 16.80 mg/kg. The Cd level observed in this study is 9.73 mg/kg higher than that reported by (Opaluwa et al., 2012) which is 0.84 mg/kg, 0.001 - 2.30 mg/kg as reported by (Adaikpo, 2013) and 0.03 - 0.37 mg/kg as reported by Nwankwoala & Ememu, (2018). However, the results were lower than 9.10 - 44.10 mg/kg reported by (Adedeji et al., 2019), and 103.60 mg/kg reported by (Fosu-Mensah et al., 2018). Soil samples from the various sites follows the order from lowest to highest BZ > BB > OG > AQ > JQ > AG > FI > NB 2 > AB > AP > NB1 > KA > AW > HL > WA > WL. The high level of Cd may be as a result prevailing human inputs such as the use of lubricating oils and/or old tires that are frequently used on the rough surfaces of the roads which increases the wearing of tyres.

The concentration of Cr in the soil was found in the range of 20.34 mg/kg to 67.50 mg/kg. The sequence of occurrence in the soil sample from lowest to highest was as follows: BZ < AG < JQ < AQ < AB < OG < BB < FI < NB2 < KA < AP < WL < HL < NB1 < AW < WA. These values obtained were in a close range to 13.21 - 41.93 mg/kg reported by (Mohammed & Folorunsho, 2015) and 6.89 - 55.43 mg/kg reported by (Abatyough et al., 2015). However, the results were higher than 1.10 mg/kg reported by (Alibrahim et al., 2017) and 0.02 - 1.56 mg/kg reported by Adaikpoh, 2013. The high concentration levels of Cr could be attributed to the proximity of the sites to the source of pollution which includes

the presence of business outlets, fueling and service stations.

Hg concentration values recorded for the soil samples ranged from ND (Not Detected) to 8.73 mg/kg. The magnitude of Hg detected in the soil samples follows the sequence from highest to lowest as AG > AB > HL > NB1 > AP > NB 2 > KA > WA > WL. These values were in a close range to that reported by Fosu-Mensah et al. (2017), which is ≤0.03 mg/kg, <0.001 mg/kg as reported by (Nwankwoala & Ememu, 2018). These heavy metal ions are also released during road transportation operations such as oil leakages, wearing out of tyres and overheating of radiators. The main medium through which these pollutants are released from vehicles is through their exhaust gases, after combustion of the different types of fuel by different vehicles.

Pb concentration levels in the soil samples from all the sites varied widely with a minimum value of 12.00 mg/kg at site BZ (control site), a maximum value of 30.21 mg/kg at sites AW and WL. The sequence of occurrence in the soil samples from the various sites follows the order BZ < OG < AQ < JQ < FI < AG < AB < BB < NB1 < AP < NB2 < KA < HL< WA < AW < WL. Similar ranges of values for lead in soil samples were reported as 16.14 - 28.59 mg/kg by (Fosu-Mensah et al., 2017), 18.1 - 28.04 mg/kg as reported by (Zhongmin et al., 2015) and 1.11 - 24.23 mg/kg as reported by (Nwankwoala & Ememu, 2018). However, the lead levels observed in this study are significantly higher than those reported by (Matthews-Amune et al., 2013) which is 0.28 - 0.60 μg/g dry weight, 14.8 - 26.67 mg/kg reported by (Osakwe & Okolie, 2015) and 17.36 - 6909 ppm as reported by (Olatunde & Onisoya, 2017). The Pb levels in roadside soil can also be attributed to high traffic of vehicles and machinery. The lower concentrations of Pb in the soil samples from other locations could be attributed to moderate human (automobile and commercial) activities in the areas.

Assessment of Soil Quality Using Pollution Indices

The results of the ecological risk assessment for all the investigated sites are tabulated from **Table 8** to **Table 9**.

Contamination factor (Cf): The Cf values were calculated using Equation (1) and was classified according to **Table 1**, the results from **Table 8**, shows that the Cf for top soil across all the sites with respect to As and Hg were insignificant. The calculated Cf values varied from 1.00 - 7.30, 1.00 - 3.33 and 1.00 - 2.50 for Cd, Cr and Pb across all the sites and showed values higher than 1 indicating a moderate contamination to considerable contamination at sites AW, HL, WL. However, site WA had Cf values for Cd above 6 indicating very high contamination. The results of Cf for Cd and Cr across all the sites were higher than that reported by (Nweke & Ukpai, 2016) and Lodhaya et al., (2017). However, the results for Pb were lower than that reported by (Ozkan et al., 2012) and (Lodhaya et al., 2017) for soil samples of Nashik District, India.

Geo-accumulation index (Igeo): The Igeo values obtained from equation (2) was classified according to **Table 2**, ranged from 0.00 - 1.36 for Cd, −0.35 - 0.69

for Cr, −0.09 - 0.86 for Pb and 0.00 for As and Hg respectively (Table 9). The total Igeo for Cr across sites BZ and AG were below 0, which indicates that the soils were uncontaminated, at sites AB, JQ, AG and AQ the values ranged from uncontaminated to moderately contaminated, at sites BB, KA, NB1, NB2, and WL the values signifies that the sites were moderately contaminated. However, sites HL, AW, and WA values ranged from moderately to heavily contaminated. For Cd, only site BZ (the control) had values less than zero (0), which indicates that the site was not contaminated. Sites HL, KA, AW, WL and WA were classified as moderately contaminated. The negative sign across all the sites for Pb shows that the sites were uncontaminated except for sites KA, NB1, NB2, WA and AW which were classified in the range of uncontaminated to moderately contaminated ($0 < \text{Igeo} < 1$). The Igeo result for As and Hg were insignificant across all the studied sites. The heavy metals responsible for high Igeo accumulation ranges in the top soil from a decreasing to an increasing order as follows; Cd > Cr > Pb > As > Hg. (Ozkan, 2012) and (Adaikpoh, 2013) reported similar Igeo values, however, the values obtained for all the metals investigated were lower compared to that reported by (Lodhaya et al., 2017) across all the sites except for Pb. This may be attributed to moderate human activities. The results obtained for Pb and Cr were higher than that reported by (Fosu-Mensah et al. 2017). The high concentrations of Pb and Cr could be attributed to human inputs (farming, waste incineration and fuel filling and service stations).

Enrichment factor (EF): The results obtained for enrichment factor as shown in Table 9, were gotten from Equation (3) and characterized according to Table 3. The EF for As and Hg across all the investigated sites was determined to be 0 which indicates that the soil is deficient to minimal enrichment. For Cd site BZ had an EF value of 1 which indicates that the soil is deficient to minimal enrichment. There was a moderate enrichment across all the sites indicating that they have EF values less than 5. Sites HL, KA, AW, WA and WL which had EF values less than 20 which indicates that the sites have significant enrichment. For Cr metal the EF values investigated shows that sites BZ, AB, AG, AQ, BB, JQ and OG have minimal enrichment values, whereas, sites AW, WA, WL, NB1, NB2, HL, KA, AP and FI had moderate enrichment, having EF values less than 5. The EF values for Pb across sites BZ, AQ, AG, AB, AP, BB, FI, JQ, NB1 And OG were less than 2 which signifies that the sites were deficient to minimal enrichment, whereas, moderate enrichment values were obtained across sites HL, KA, NB2, AW, WA and WL. Aluminum (Al) was used as a reference element (Seng-Chee & Norhayati, 2016). Reference elements are elements which are stable and are characterized by non-vertical mobility and/or degradation phenomena (Lodhaya et al., 2017). Similar results were reported by (Wuana et al., 2019) and (Adedeji et al., 2019). The EF results obtained for Pb, Cd, As and Hg were lower than that reported by (Ozkan, 2012), (Fosu-Mensah et al., 2017), this may be due to moderate anthropogenic activities, however, higher values obtained for Cr, Cd and Pb were higher than the values reported by (Nweke & Ukpai, 2016) and (Lod-

haya et al., 2017). These high values could be due to prevailing human activities.

Pollution load index (PLI): The PLI value for this study was calculated using Equation (4) and classified according to **Table 4**. **Table 8**, shows the results of the PLI of the five heavy metals studies across the sites, the values were in the range of 1.00 - 2.23. Only site BZ (control) had a PLI value equal to 1, which indicates that only baseline levels of pollutants are present (PLI = 1). Other sites have PLI values from 1 above (>1) which shows signs of pollution or deterioration of the soil quality. Similar results were obtained by (Lodhaya et al. 2017) and (Fosu-Mensah et al., 2017). However, the result investigated was higher than that reported by (Mmolawa et al., 2011). This implies that inputs from anthropogenic sources attributed to increase in human activities and vehicular emissions.

Modified degree of contamination: The mCd values were obtained using Equation (5) which was derived from the addition of all the heavy metals analyzed for each site investigated. From **Table 8**, sites AB, AG, AQ, BZ, BB, FI, JQ, AP, NB1, NB2 and OG had nil to low degree of contamination. These results were in line with the findings of (Wuana et al., 2019), for toxic metals from farmland soil in Makurdi. Sites HL, AW, WA and WL had moderate degree of contamination across the sites. However, the results obtained were lower than that investigated by (Fosu-Mensah et al., 2017) and (Nwankwoala & Ememu, 2018).

Nemerow pollution index (P_{nemerow}): The results obtained were gotten using Equation (6). The results ranged from 0.70 - 5.47. **Table 8**, shows that site BZ (control) had a value of 0.7 which falls within the warning limit. Sites AQ, BB, FI and OG were slightly polluted, sites AB, AG, HL and JQ were moderately polluted and sites AP, KA, NB1, NB2, AW, WA and WL were highly polluted, the terminologies used were from **Table 6**. Similar result was reported by (Wuana et al., 2019). Similarly, the results were also lower than that reported by (Nwankwoala & Ememu, 2018). However, the results deviated slightly from that reported by (Lodhaya et al., 2017). This deviation may be attributed to proximity of the area to pollutants coupled with high vehicular movement.

6. Conclusion

The study provides useful data on the contamination of top soil in relation to land use patterns in the study area and may form basis for land use planning. The findings have revealed that the concentrations of the metals in the top soil samples were arranged in the sequence from increasing to decreasing order thus; Cr > Pb > Cd > Hg > As. From the computation of contamination factor (Cf), ecological risk (Er), enrichment factor (EF), pollution load index (PLI), Geo-accumulation index (Igeo), modified degree of contamination (mCd), potential ecological risk (PERI) and nemerow pollution index, it was observed that the pollution levels of As and Hg were insignificant, while, the level of pollution caused by Cd, Cr and Pb ranged from low level of contamination to high level of

contamination across the investigated sites, except, for the control site (BZ) whose pollution level was insignificant with respect to the heavy metals studied. Based on the results from this study, it confirms human activities as the source of pollution in the area under study. Therefore, continuous monitoring is necessary to identify the degree of heavy metal contamination and select possible remediation measures in order to manage land use in relation to anthropogenic activities.

Conflicts of Interest

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

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