BASELINE LEVELS OF SOME HEAVY METALS IN SOILS OF SOUTHERN KADUNA, KADUNA STATE – NIGERIA

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Abstract

The baseline levels of lead, manganese, copper, zinc, cadmium, and nickel were determined in the top soils of the study area in order to define benchmark concentrations for these elements as a basis for future environmental monitoring and pollution control studies. Ten (10) soil samples each were randomly collected from eight (8) local government areas giving a total of eighty (80) soil samples. The samples were subjected to standard methods and analyzed using the flame atomic absorption spectrophotometer (AAS-HP, Serial Number: MY14470001). The mean concentrations of these metals were found to be 19.19±2.13, 26.96±1.69, 16.31±2.03, 39.95±9.91, 2.09±1.31 and 8.20±2.98mgkg^{-1} for Pb, Mn, Cu, Zn, Cd, and Ni respectively. Also, the mean values of pH and percentage Organic Carbon were 6.01±1.19 and 2.08±1.75% respectively. Analysis of variance (ANOVA) showed that there were significant differences ($p< 0.05$) in the concentrations of the measured metals in the various local government areas of the study area. Also, the concentrations of analyzed metals significantly correlated suggesting that, similar processes might control their associations in the soils, and might also have a common source of origin. Apparently, the soil environments are yet to be impacted negatively by these heavy metals because their levels were within the natural concentration levels and are therefore regarded as not polluted.

Keywords: Background Levels, Benchmark, Soil, Polluted, Heavy metals, Southern Kaduna

Introduction

Environmental contamination by heavy metals has become a world-wide problem in recent years due to the fact that unlike some other pollutants, they are not biodegradable. As a result, they are not detoxified but are bio accumulated. They are generally found in small amounts and become toxic over determined concentration thresholds. Some of these at low concentrations are essential to life cycle acting as micro-nutrients and they include cobalt, chromium, copper, iron, manganese, nickel and zinc (Camilotti *et al.,*2007; Diez, 2006). The second group is composed of those that do not have known biological functions and after determined levels cause serious dysfunctions in organisms and they include cadmium, lead, arsenic and mercury (Recatala *et al.,* 2010).

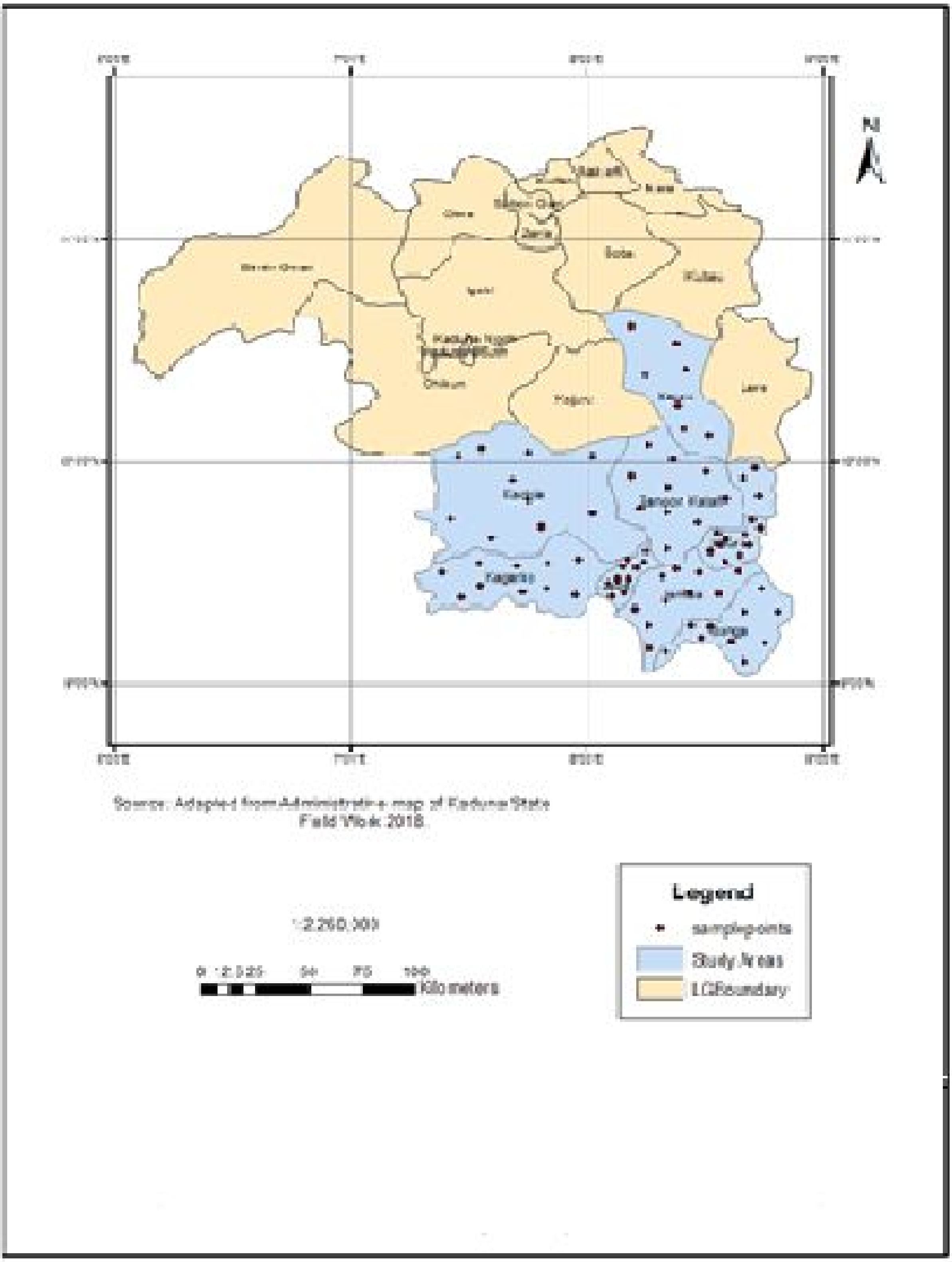
The unconsolidated minerals and organic materials found on the immediate earth surface that serves as a natural medium for plants growth and other developmental activities make up what is referred to as soil (Haliru*et al*., 2014). It is composed of mineral constituents, organic matter (humus), living organisms, air and waters (Keestra *etal*., 2016; Keestra *et al*., 2012). In general, heavy metals occur naturally in soils as a result of geological processes such as alteration and erosion of the geologic underground materials (Kabir*et al*., 2012; Moor *et al,* 2001). Besides the parent material, sources of contamination in soils are multifarious, and include agricultural and industrial pollution (Moor, 2001). The topsoil layer contains the largest amount of pollutants which mainly depend on the adsorption properties of the soil matter while the solubility of the heavy metal ions in soils is mainly influenced by many factors such as the pH, conductivity, and moisture content (Rakesh & Raju, 2013). According to Rodrigo-Comino and Cerda (2018) high rates of run-off and soil losses are the main driving forces of transport of pollutants in soils.

Baseline refers to the natural variation in the concentration of an element in the surface environment at a determined place and time and the concept of baseline includes natural geographic concentrations known as background levels and the diffused anthropogenic contribution in soils. According to Garcia *et al.* (2010) and Matchullat *et al.* (2000), background level is a measure that is used to differentiate between the concentration of the natural compound and the concentrations with an anthropogenic influence in a given environmental sample. The investigation of the baseline of a territory represents a measure of the geochemical variations of its surface formations (rocks and soils) and is considered of great interest, not only from a scientific and mining point of view, but also constitutes a very important tool for environmental planning, environmental health, and sustainable development policies worldwide (Salminen *&* Gregorauskiene*,* 2000).

Materials and Methods

Study Area

The study area is located within Southern Kaduna area which lies between longitude 5 and 7^0east and latitude 9^0 43'N and 11^0 32'N.The area comprises eight of (8) local government areas namely: Kachia, Kagarko, Jaba, Jema’a, Sanga, Kaura, Kauru and ZangonKataf(Figure1).



Source: Adapted from Administrative map of Kaduna State
Field Work 2018

Fig. 2.1: Map of Kaduna State Showing the Study Area and Sampling Points

Sample Collection and Pre-treatment

Soil samples were collected from five (5) different locations representing the North, South, Central, East and Western part of the local government areas within the study area.

Sampling sites of low-anthropogenic activities were chosen and at each point within a location, approximately 0.5kg soil was collected at a depth of 0-20cm with the help of a garden shovel cleaned at intervals with nitric acid. A total of eighty (80) soil samples were collected and the exact collection point of each sample recorded with a Global Positioning System (Garmin GPS 60) reading. Samples taken were transferred to clean, well labeled polyethylene storage bags for later analysis. In the Laboratory, the soil samples were air-dried; gravels and plant roots were removed. The soil samples free of plant roots and gravels were then crushed with a wooden mortar and passed through a 20-mesh sieve and put into clean well labeled polyethylene bags, stored at room temperature for later chemical analyses.

Sample Digestion

Exactly 1.0g of well mixed samples of soil was weighed into a 250cm^3 glass beaker covered with a watch glass and digested with 24cm^3 of aqua-regia (1:3 HNO_3-HCl, v/v) on a hot plate for 3hrs at 110°C. After evaporation to near dryness, the digest was diluted with 10 cm^3 of 2% (v/v) nitric acid, filtered using Whatman No.42 filter paper and made up to mark in a 100cm^3 volumetric flask with distilled water (Begum *et al.,* 2009).

Determination of Soil pH

In determining the pH of the soil samples, a mixture of soil and distilled water was prepared by weighing 20g of fine grained (pulverized) soil into a glass beaker and 20cm^3 of de-ionized water was added and stirred gently to enhance Hydrogen ions release from soil. The soil pH was measured after the resulting mixtures were allowed to stand for 30 minutes using a pH meter (Stephen & Oladele, 2012).

Determination of Organic Carbon in Soil

Soil organic carbon was determined by weighing 5.0g of the soil sample into 250cm^3 Teflon beaker. Each sample was subjected to rapid dichromate oxidation by addition of 50cm^{3}of 0.5moldm^{-3} $K_2Cr_2O_7$ and 2.5cm^3 concentrated H_2SO_4 in 5% $FeSO_4$. The resulting solution was swirled and allowed to stand for a while to reduce the heat generated. The sample was boiled for 30 minutes at 150°C and water added to halt the reaction. 10cm^{3}of H_3PO_4 was added to each of the digested mix after cooling to eliminate interference from iron(III) ions that may be present. Excess dichromate ions was titrated with 0.25moldm^{-3} $(NH_4)_2Fe(SO_4)_2.6H_2O$ using barium diphenylamine sulphonate as indicator. The percentage organic carbon was calculated as follows:

Organic Carbon (%) = $(B - S) \times (0.0006)/m \times 100$

Where: B = volume of ferrous solution used in the blank titration,
S = volume of ferrous solution used in the sample titration,
m = the mass of sample in grammes used in the analysis (Walkley & Black, 1934).

Sample Analysis

The flame atomic absorption spectrophotometer machine (AAS-HP, Serial Number: MY14470001) was used in the analysis of the digested soil samples for the determination of the heavy metals. Its parameters were set according to the specifications given in the manufacturer's manual. The ASS machine had an automatic picking meter that indicated when the optimum conditions had been realized.

Method Validation

The digestion method and atomic absorption spectroscopy analysis were validated by recovery method. One gramme (1.0g) of randomly selected soil powder was spiked with three different concentrations of heavy metals one at a time (1.0, 1.5, 2.0ppm). This was followed by the digestion of the spiked samples and determination of metal concentration using the AAS. Blank or unspiked samples were digested and run through the same AAS. The amount that was recovered after digestion of the spiked samples was used to calculate percentage recovery as follows:

Recovery(% $\frac{\text{recovery concentration}}{\text{spike concentration}}$ 100(Al-weher, 2008)................................ (1)

Data Analyses

Statistical analyses were conducted on the data collected from chemical and instrumental analysis from this study using the Microsoft Excel computer software package (Microsoft Corporation, 2013 version). Geometric mean (GM) and Geometric Standard Deviation (GSD) were used for the baseline establishment of heavy metal concentrations in soils using the equation below:

$$GM = \sqrt[n]{x_1, x_2 ......x_n} \quad GSD = \exp\left[\sqrt{\frac{\Sigma_{i=1}^{n}\left(In\frac{x_i}{GM}\right)^2}{n}}\right] .... (2)$$

Where, n is the number of observations (x_1,x_2)

Lower limits of baseline concentration were defined as (GM/ GSD^2), while the upper limits were defined as (GM *GSD^2), (Pendias & Pendias, 2001; Chen *et al.,* 1999). Analysis of Variance (ANOVA) was performed to compare mean metal concentrations among the various local government areas in the study area. Also, simple correlation analysis was used to relate element concentrations to soil properties and among themselves.

Results

Table 1 shows the summary of metal concentrations, pH and % OC in the surface soil. The soils of Southern Kaduna area are generally red brown to red yellow tropical ferruginous in nature. The arithmetic mean and arithmetic standard deviation concentrations (mgkg^{-1}) of the heavy metals (ranges in parenthesis) detected in the soils were: Pb: 23.07 ± 11.31 (0.70-51.20); Mn: 30.69±18.39 (10.00-89.70); Cu: 20.01±14.17 (1.20-73.00); Zn: 50.81±47.74 (13.90-310.90); Cd: 2.03±0.58 (0.90-3.20); Ni: 13.48±14.40 (0.10-64.90) respectively. The Geometric mean and Geometric Standard Deviation concentrations (mgkg^{-1}) of the heavy metals were: Pb: 19.19±2.313; Mn: 26.96±1.69; Cu: 16.31±2.03; Zn: 39.95±1.91; Cd: 2.09±1.31; Ni: 8.20±2.98 respectively. The arithmetic mean and arithmetic standard deviation for the pH and the percentage organic carbon detected in the soils (ranges in parenthesis) were, 6.10±1.03 (4.05-7.95) and 2.39±1.19 (0.50-5.60) respectively. Also, the Geometric mean and Geometric standard deviation for the pH and percentage organic carbon were, 6.01±1.19 and.08±1.75 respectively.

Table 1: Concentrations of Heavy metals (mgkg^{-1}), pH and percentage organic carbon in Southern Kaduna surface soil

Element	Range	Median	AM±ASD	GM±GSD
Pb (mgkg^{-1})	0.70–51.20	23.45	23.07±11.31	19.19±2.13
Mn (mgkg^{-1})	10.00-89.70	24.00	30.69±18.39	26.96±1.69
Cu (mgkg^{-1})	1.20-73.00	15.70	20.01±14.17	16.31±2.03
Zn (mgkg^{-1})	13.90-310.90	35.04	50.81±47.74	39.95±9.91
Cd(mgkg^{-1})	0.90-3.20	2.10	2.03±0.58	2.09±1.31
Ni (mgkg^{-1})	0.10-64.90	8.00	13.48±14.40	8.20±2.98
pH	4.05-7.95	6.27	6.10±1.03	6.01±1.19
%OC	0.50-5.60	2.31	2.39±1.19	2.08±1.75

AM = Arithmetic Mean, ASD = Arithmetic Standard Deviation, GM = Geometric Mean, GSD = Geometric Standard Deviation, OC = Organic Carbon

Table 2: Single factor ANOVA for Lead

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	6271.857	7	895.979	16.170	4.491	2.126
Within Groups	4432.7	80	55.4087			
Total	10704.56	87				

Result is significant at ($p < 0.05$)

Table 3: Single factor ANOVA for Manganese

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	5246.805	7	749.543	2.490	0.022	2.126
Within Groups	24073.21	80	300.915			
Total	29320.01	87				

Result is significant at ($p < 0.05$)

Table 4: Single factor ANOVA for Copper

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	6509.098	7	929.871	6.737	2.806	2.126
Within Groups	11040.62	80	138.007			
Total	17549.72	87				

Result is significant at ($p < 0.05$)

Table 5: Single factor ANOVA for Zinc

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	46086.93	7	6583.848	3.431	0.002	2.126
Within Groups	153488.1	80	1918.602			
Total	199575.1	87				

Result is significant at ($p < 0.05$)

Table 6: Single factor ANOVA for Cadmium

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	15.20182	7	2.171	13.54227	2.041	2.126
Within Groups	12.82909	80	0.160			
Total	28.03091	87				

Result is significant at ($p < 0.05$)

Table 7: Single factor ANOVA for Nickel

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	12519.71	7	1788.53	27.90549	4.98E-19	2.126324
Within Groups	5127.393	80	64.09241			
Total	17647.1	87				

Result is significant at ($p < 0.05$)

Table 8: Correlation matrix, between heavy metals pH and organic carbon in surface soil samples of Southern Kaduna

	Pb	Mn	Cu	Zn	Cd	Ni	pH	OC
Pb	1							
Mn	0.12	1						
Cu	0.15	0.46*	1					
Zn	0.16	0.47*	0.45*	1				
Cd	0.06	0.49	0.23	0.49	1			
Ni	0.21	0.25	0.48*	0.73*	0.40*	1		
pH	0.49*	0.47*	0.51*	0.54*	0.46*	0.48*	1	
OC	0.46*	0.49*	0.54*	0.59*	0.52*	0.47*	0.93*	1

OC: Organic Carbon *: positive correlation

Discussion

Recovery study was carried out on spiked soil samples in order to determine the accuracy and precision of the atomic absorption spectrophotometer used in the measurement of the heavy metal concentrations in the soil samples, as well as to validate the digestion method used in the extraction of the heavy metals in the soils matrix. The result obtained from the data analyzed showed that the mean percent recoveries for the measured metals in the matrix spike samples ranged from 95.29 to 99.12 %. All the recovery values therefore, were within the acceptable range of 80 – 120 % for metal analysis as proposed by Christian (2003).

The results of the heavy metal concentrations in soils in the study area as presented in table 1 show that the concentration levels of zinc were the highest in respect of the metals measured. The concentration distribution sequence trend were: Zn >Mn>Pb> Cu > Ni > Cd respectively; and it is consistent with the findings of Stephen and Oladele (2012), on Itakpe soils of North Central Nigeria.

The concentration of lead in this study (19.19 ± 2.13 mgkg^{-1}) was found to be in close proximity with the concentration of lead reported by Bradford *et al.* (1996) and Wei *et al.* (1990), for California (21.70 mgkg^{-1}) and China (23. 6 mgkg^{-1}) respectively. However, the concentration of lead was found to be relatively higher than the values reported by Ma *et al.* (1997) and Shaclette and Boerngen (1984) who reported values for Florida and U. S. A. soils to be 4.10 mgkg^{-1}and 16.00 mgkg^{-1}respectively.

Ma *et al.* (1997) reported the concentration of manganese for Florida top soils to be 25.00 mgkg^{-1}which is consistent with the concentration recorded (26.96 ± 1.69 mgkg^{-1}) in this study. The result detected for manganese in this study was however far below the concentration reported by Ming *et al.*, (1999).

Copper concentration (16.31 ± 2.03 mgkg^{-1}) detected in this study is in agreement with the result reported by Shacklette and Boerngen (1984) for USA soils (17.00 mgkg^{-1}). However, the concentration of copper in this study was below the report of Stephen and Oladele, (2012) (51.50 ± 7.35 mgkg^{-1}) and above the concentration reported by Zhifeng *et al.* (2008) (11.20 ± 1.60 mgkg^{-1}).

The zinc concentration as reported by Zhifeng *et al.* (2008) is 39.70 ± 1.40 mgkg^{-1} which is in close agreement with the result obtained in this study (39.95 ± 1.91 mgkg^{-1}), but it is below the 67.70 mgkg^{-1}reported by Wei *et al.* (1990) for China soils and 145 mgkg^{-1} for California soils as reported by Ma *et al.* (1997).

Cadmium concentration in this study was found to be 2.09 ± 1.31 mgkg^{-1}which was far above the 0.16 ± 0.05 mgkg-^{1} concentration reported by Stephen and Oladele (2012) Itakpe soils and 0.04 ± 1.70 mgkg^{-1} concentration reported by Zhifeng*et al.* (2008) for Guangdong soils. However, the result of Cadmium in this study was in close agreement with the 1.47 mgkg^{-1} concentration reported by Sanjeevani *et al.* (2013).

Reported concentration of nickel (9.08 ± 2.31mgkg^{-1}) by Chen *et al.* (1999) for Florida soils was in close agreement with the result obtained in this study (8.20 ± 2.98 mgkg^{-1}) but was below the 13.00 mgkg^{-1} concentration reported by Shacklette and Boerngen (1984) for USA soils and the 23.60 mgkg^{-1} concentration reported by Wei *et al.* (1990) for China soils.

According to He *et al.* (2004), pH has a significant influence on metals solubility and soil anion exchange capacity and hence the relative abundance of heavy metals in soils. Also, Biney *et al.* (1994) reported that properties of soil such as pH, organic carbon, particle size, clay mineral composition partly account also for the concentrations of heavy metals in soils. Therefore, the sorption capacity of soils is a function of soil organic and clay minerals, and this defines the retention capacity of soils.

In this study, Analysis of Variance was performed on the concentration values of the heavy metals using the Microsoft Excel computer software package (Microsoft Corporation, 2013 version) in order to compare the mean metal concentrations among the various local government areas in the study area as presented in tables 2-7. According to the one-way analysis of variance, the results show that significant differences ($p < 0.05$) were observed between the concentrations of the measured heavy metals in the various local government areas in the study area. This suggests that, the heavy metals were heterogeneously distributed in the study area.

Table 8 shows the correlation matrix between heavy metals, pH and organic carbon in surface soil samples of Southern Kaduna. From this study, all the heavy metals measured correlated significantly with pH indicating that their availability in all the sampled locations might be from the same source as evident from the pH values which ranged from 4.05 – 7.95 across all the sample locations and sites. It was also observed that there was a significant correlation ($p < 0.05$) between the levels of heavy metals in soils and organic carbon levels with correlation coefficient for Cd, $\gamma = 0.52$, Mn, $\gamma = 0.49$, Zn, $\gamma = 59$, Cu, $\gamma = 0.54$, Pb, $\gamma = 0.46$, and Ni, $\gamma = 0.47$. Adamu and Nganje (2010), reported that strong correlations between elements imply similar geochemical controls in the surface environment and poor correlation of heavy metals with each other implies different sources of origin. In this regard, a positive correlation was observed between Zn and Ni ($\gamma = 0.73$), Cu and Ni ($\gamma = 0.48$), Cd and Zn ($\gamma = 0.49$), Cu and Zn ($\gamma = 0.45$), Cu and Mn ($\gamma = 0.46$), the correlations between these metals observed might suggest the metals might associate mainly with the mineral phase in the soils.

Conclusion

The concentration levels of Pb, Mn, Cu, Zn, Cd and Ni in soils around Southern Kaduna were found to be low and within natural concentration levels. The soils are not considered as contaminated, thus, the soil environment around the study area are yet to be impacted negatively by heavy metals. The concentration distribution sequence trend were: Zn >Mn>Pb> Cu > Ni > Cd respectively. The result from this research work obtained from analysis of variance (ANOVA) revealed that there was a significant difference ($p > 0.05$) in the distribution pattern of heavy metals across the various local government areas in the study area. Also, this research work revealed significant correlation coefficients ($p > 0.05$) among most of the heavy metals measured suggesting, that similar processes might control their associations in the soils and might also have a common source of origin. The study has revealed the baseline concentration levels of Pb, Zn, Cd, Cu, Ni and Mn in soils around Southern Kaduna area of Kaduna State, Nigeria, which was hitherto non-existent. This baseline concentration data will serve as a bench mark for other researchers in the future.

Recommendations

Heavy metals occupy a special position in soil chemistry because of the very important physiological roles they play in nature. The investigation of the baseline of a territory represents a measure of the geochemical variation of its surface formations and is considered of great interest; not only from a scientific and mining point of view, but also constitutes a very important tool for environmental planning, environmental health and sustainable development policies worldwide. Therefore, it is recommendations that:

(i). Research should be carried out regularly by government agencies so as to develop an environmental monitoring and management programme for heavy metals in the study area.
(ii). Further research should be carried out regularly to ascertain the level of heavy metals pollution in the soil environment in the study area.
(iii). Research on soil heavy metals in the study area should be done at greater soil depth.

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