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Assessment of Heavy Metals in Soil of Automobile Workshops in Federal Capital Territory Abuja, Nigeria

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Abstract: *Heavy metals contamination in soil is of concern due to food safety issues and possible health risks. This study aimed at assessing the concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in soil of five (5) automobile workshops in the Federal Capital Territory of Nigeria (FCT). Soil samples were collected between September 2016 rainy season and March 2017 dry season. Heavy metals concentrations in soil were quantified using Atomic Absorption Spectrophotometer. In dry season, the concentration of heavy metals (mg/kg) in soil samples ranged from 0.29±0.00 - 0.58±0.00 for Cd, Cr: 1.45±0.00 – 4.81±0.02, Cu: 0.76±0.00 – 2.96±0.00, Fe: 651.43±0.01- 682.61±0.02, Mn: 14.81±0.00 - 26.24±0.00, Ni: 2.11±0.00 - 3.18±0.00, Pb: 2.81±0.00 - 10.94±0.00 and Zn: 11.93±0.00 - 35.36±0.00. However in wet season, the levels ranged from 0.07±0.00 - 0.29±0.00 for Cd, Cr: 1.06±0.00 - 1.45±0.00, Cu: 0.35± 0.00 - 1.68± 0.00, Fe: 534.41±0.00 - 549.28±0.01, Mn: 9.90±0.00 - 31.59±0.00, Ni: 0.87±0.00 - 2.22±0.00, Pb: 2.34±0.00 - 5.00±0.00 and Zn: 6.19±0.01- 32.06±0.00. Iron had the highest level of concentration while cadmium recorded the lowest in the soil. Heavy metal concentrations were higher in dry season than in rainy season. The levels of heavy metals obtained were within WHO[1] permissible limits for soil.*

Keywords: *Assessment, Heavy metals, Soil, Automobile Workshop, FCT Abuja*

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I. Introduction

Soil is a complex mixture of organic and inorganic matter, with different components that determine its physical, chemical and biological properties. Soil is a major reservoir for contaminants as it is capable of binding various chemicals, these chemicals can occur in different forms in soil and different forces keep them bond to soil particles[2]. The properties of the soil may change due to climate change, but mostly due to anthropogenic impact.

Heavy metals are chemical elements having atomic number more than 20 with density greater than 5g/cm^3 found in soils, rocks and freshwater ecosystems[3, 4]. They constitute heterogeneous group of elements which vary widely in their chemical properties and biological functions. They are non-biodegradable, having long biological half-lives, difficult to eliminate naturally from the environment and high potentials for accumulation in different body organs leading to unwanted side effects[5]. In Nigeria, one of the major sources of increase in heavy metals concentration in the soil ecosystem is due to auto mechanic activities[6]. Levels of heavy metals in the environment have increased greatly in the past decades due to human activities. Karu, Nyanya, Kugbo, Apo and Lugbe areas in Federal Capital Territory (F.C.T) have experienced increase in the number of auto-mobile workshops as a result of increase in population and may not be an exception to the foregoing heavy metal contamination problem. Heavy metals associated with the activities in automobile workshops such as fluid leakage, component wear, engine oils and corrosion of metals, painting of vehicles and tyres vulcanizing are washed into soil which may contribute to high levels of these metals in soil causing pollution. Excessive accumulation of heavy metals in agricultural soils not only results in environmental contamination, but also elevates heavy metal uptake by crops which affects food quality and safety[7].

Accumulating high concentration of heavy metals in the environment may cause health problems which includes vomiting, stomach cramps, skin irritations, nausea, anemia, cardiovascular, kidney, blood, nervous, and bone diseases[8].

II. Materials and Methods

Study Area

Five different automobile workshops in F.C.T Abuja were selected for this study. Abuja is the capital of Nigeria and shares boundaries with Kogi State, Niger State and Nasarawa State. The sampling locations were at Karu, Kugbo Nyanya, Apo and Lugbe represented by stations 1 – 5 respectively (Figure 1). All the stations have typical characteristics of automobile work sites, such as patches of waste engine oil on the ground, scrap

metals, discarded engine oil containers and paint cans, among others. The control station is an uncontaminated site with no mechanic activity carried out on the soil of the land before.

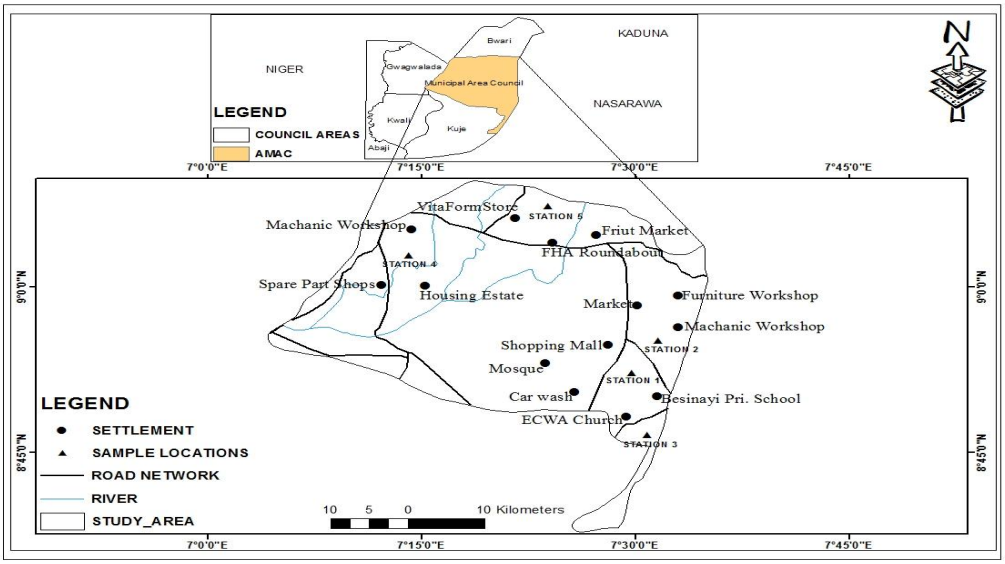

Figure 1: Map of FCT Abuja showing the study area

Surface soil samples (0-10cm) were collected from the five different sites using a hand auger. Collection of the soil samples was done at twelve different points of a particular location of the sites and transferred into polyethylene bags with tight plastic clips, labelled properly and then transported to the laboratory. The subsamples were well mixed together to create a single composite sample for each of the sites and then air dried for two (2) weeks in the laboratory. These samples were then crushed and sieved through a 2mm mesh sieve to obtain fine particles and kept for acid digestion.

Sample Digestion

Soil sample (1.00 g) was weighed into a 250 cm^3 beaker for digestion and 10 cm^3 of concentrated HNO_3 added, then heated at 95 ^{0}C. This was refluxed after cooling, with repeated addition of HNO_3 until no brown fumes were given off by the sample. The volume of the solution was allowed to reduce to 5 cm^3 by evaporation. 10 cm^3 H_2O_2 was added slowly without allowing any losses after cooling the mixture. 10 cm^3 of HCl was added to the mixture and refluxed at 95 ^{0}C for 15 minutes. The digest obtained was filtered using Whatman No. 41 filter paper. The filtrate was diluted, made up to 100 cm^3 volume in a volumetric flask and stored for analyses.[9]

Determination of Physicochemical Parameters of the Soil

pH

Ground and sieved soil sample (10.00 g) was weighed and transferred into a beaker, 10 cm^3 of deionised water was added and the mixture was stirred to obtain slurry. The mixture was allowed to stand for an hour, stirred at every 10 to 15 minutes. A calibrated pH meter with glass-calomel electrode was used for the pH measurement. Prior to the pH determination, the prepared standard buffer solutions were used for the pH calibration. The pH meter electrode was thoroughly rinsed with deionised water after immersing into each of the soil solution[10].

Cation exchange capacity

Soil sample (25.0 g) was weighed into a 500cm^3 Erlenmeyer flask and 125 cm^3 of 1 mole $dm^{-3}NH_4OAc$ was added and mixed thoroughly, then allowed to stand overnight.

A 5.5 cm^3 Buchner funnel was fitted with retentive filter paper which was moisten and light suctioned, and the soil transferred. The soil was gently washed four times with 25cm^3 additions of the NH_4OAc, allowing each addition to filter through but not allowing the soil to crack or dry. Suction was applied only to ensure slow filtering. The leachate was discarded. The soil was further washed with eight separate additions of 95% ethanol to remove excess saturating solution. The adsorbed NH_4 was extracted by leaching the soil with eight separate 25cm^3 additions of 1 mole dm^{-3}KCl. The soil was discarded, and the leachate transferred to a 250 cm^3 volumetric flask. Then the volume was diluted with additional KCl.

The concentration of NH_4-N in the KCl extract was determined by colorimetry. Also NH_4-N was determined in the original KCl extracting solution (blank) to adjust for possible NH_4-N contamination in this reagent[11].
Calculations:

$$\text{CEC (cmolc/kg)} = \frac{(\text{NH 4–N in extract} - \text{NH 4–N in blank})}{14} \quad (2.1)$$

Where NH_4-N is reported in mg N/L

$$\text{CEC (cmol}_c\text{/kg)} = \frac{(\text{NH 4–N in extract} - \text{NH 4–N in blank})}{18} \quad (2.2)$$

Where NH_4-N is reported in mg NH_4/L

Organic Matter (OM)

Organic Matter was determined using Walkley-Black Method**.** Dry soil sample (1.00 g) was weighed and transferred into a 500 cm^3 Erlenmeyer flask, 10 cm^3 of 0.167 moles dm^{-3} potassium dichromate ($K_2Cr_2O_7$) solution was added using pipette followed by the addition of 20 cm^3 of concentrated H_2SO_4 using a dispenser and the mixture was swirled gently to mix. The mixture was allowed to stand for 30 minutes and diluted with 200 cm^3 of deionised water. Phosphoric acid (10 cm^3) was added followed by 0.2 g sodium fluoride (NaF). (The H_3PO_4 and NaF were added to complex Fe^{3+} which would interfere with the titration end point). This was followed by the addition of 10 drops ferroin indicator. The mixture was titrated with 0.5 moles dm^{-3} Fe^{2+} solution, the colour of the solution at the beginning was yellow-orange to dark green, while the colour changed to wine red at the end point. A blank was prepared and titrated in the same manner but without the soil[12].

$$\% \text{ Organic Matter} = 10[1- (S \div B)] \times 0.67 \quad (2.3)$$

Where S is sample titration, B is blank titration, 10 is conversion factor for units. 0.67 is a factor derived from the conversion of % organic carbon to % organic matter.

Soil Salinity

Soil salinity was determined weighing soil sample (20 g) into a 250cm^3 beaker. 20 $cm^3$of deionized water was added to the beaker and stirred thoroughly with glass rod for about 1 hour until well mixed, the suspension was allowed to settle. The EC of the supernatant was measured at 25^0C with a conductivity meter. The conductivity meter probe was properly rinsed with deionized water before and after reading[13].

Quantification of Heavy Metals in the Samples

Heavy metal concentrations of Fe, Cu, Zn, Cd, Mn, Ni, Pb, and Cr in the soil samples were determined in triplicates using an Atomic Absorption Spectrophotometer, (ASS-6800 SHIMADZU JAPAN)

Statistical Analysis

Simple statistics such as mean and standard deviation of values were calculated.

III. Results

Table 1: Shows the levels of the physicochemical parameters of soil samples. The values of the pH of soils in the vicinity of automobile workshops ranged from 5.10 to 6.00 in wet season while that of control is 7.05. In dry season the values ranged from 5.00 to 5.60 with the control site having 6.90. The electrical conductivity (EC) of the soil ranged from 49.20 to 75.12 µS/cm in wet season with Apo, Kugbo and Karu soils having values relatively higher than that of Lugbe and Nyanya, the control soil had lower values compared to the study areas. In dry season, the values ranged from 51.00 to 76.56 µS/cm. Organic matter of the soil samples ranged from 4.90 to 6.50 %, in the wet season, with Kugbo soil having the highest value followed by Apo and Karu. The values ranged from 2.89 to 5.96 % in the dry season. The control samples had the lowest values in both seasons. Cation exchange capacity (CEC) values ranged from 8.40 to 9.50 cmol/kg in the dry season, while it ranged from 7.08 to 7.92 cmol/kg in the wet season.

Table 1: Shows Physicochemical Parameters of Soil Samples

Sampling site	Season	pH	EC (µS/cm)	OM%	CEC(cmol/kg)
Karu	**wet**	5.60 ± 0.05	70.00 ± 0.08	6.10 ± 0.52	7.82 ± 0.03
	dry	5.40 ± 0.06	68.14 ± 0.06	4.67 ± 0.42	8.58 ± 0.06
Kugbo	**wet**	5.12 ± 0.04	71.10 ± 0.06	6.50 ± 0.58	7.80 ± 0.05
	dry	5.00 ± 0.06	71.59 ± 0.06	5.96 ± 0.51	8.90 ± 0.06
Nyanya	**wet**	6.00 ± 0.03	49.20 ± 0.07	4.92 ± 0.58	7.92 ± 0.05
	dry	5.60 ± 0.05	51.00 ± 0.05	3.13 ± 0.23	9.50 ± 0.06
Apo	**wet**	5.10 ± 0.04	75.12 ± 0.06	6.11 ± 0.30	7.47 ± 0.05
	dry	5.00 ± 0.06	76.56 ± 0.07	4.10 ± 0.56	8.40 ± 0.06
Lugbe	**wet**	5.70 ± 0.04	64.11 ± 0.07	4.90 ± 0.54	7.08 ± 0.06
	dry	5.20 ± 0.06	66.98 ± 0.04	2.89 ± 0.40	9.02 ± 0.05
Control	**wet**	7.05 ± 0.05	29.10 ± 0.06	1.95 ± 0.58	7.30 ± 0.05
	dry	6.90 ± 0.06	28.57 ± 0.06	1.80 ± 0.46	9.34 ± 0.05

EC = Electrical conductivity, CEC = Cation exchange capacity, OM = Organic matter

Table 2: Indicates heavy metal concentrations in soil samples obtained from the five study areas for the dry season. The contents of Fe, Cu, Zn, Cd, Mn, Ni, Pb, and Cr varied from 651.44±0.01 to 682.61±0.02, 0.76±0.00 to 2.96±0.00, 11.93±0.00 to 35.36±0.00, 0.29±0.00 to 0.58±0.00, 14.81±0.00 to 26.93±0.00, 2.11±0.00 to 3.18±0.00, 2.81±0.00 to 10.94±0.00, and 1.45±0.00 to 4.81±0.02

Table 2: Shows Heavy Metal Concentrations in Soil Samples for the dry season (mg/kg)

Sampling sites	Fe	Cu	Zn	Cd
Karu	682.61±0.02	1.55±0.00	17.35±0.00	0.29±0.00
Kugbo	651.43±0.01	2.96±0.00	23.12±0.01	0.40±0.00
Nyanya	681.68±0.01	0.76±0.00	11.93±0.00	0.43±0.00
Apo	675.12±0.02	0.90±0.00	35.36±0.00	0.58±0.00
Lugbe	678.30±0.01	1.72±0.00	13.09±0.02	0.34±0.00
Control	452.33±0.02	0.05±0.00	6.42±0.01	0.13±0.00

Mn	Ni	Pb	Cr
26.24±0.00	3.11±0.00	8.82±0.00	1.45±0.00
15.62±0.00	2.11±0.00	10.69±0.00	3.61±0.00
26.93±0.00	3.18±0.00	10.94±0.00	2.79±0.00
19.44±0.00	3.15±0.00	4.00±0.00	4.81±0.02
14.81±0.00	2.70±0.00	2.81±0.00	4.11±0.00
6.92±0.00	1.60±0.00	2.38±0.00	1.38±0.00

Table 3: Presents heavy metal concentrations in soil samples obtained from the five study areas for the wet season. The concentrations of Fe, Cu, Zn, Cd, Mn, Ni, Pb, and Cr ranged from 534.41±0.00 to 549.28±0.01, 0.35±0.00 to 1.68±0.00, 6.19±0.01 to 32.06±0.00, 0.07±0.00 to 0.29±0.01, 9.90±0.00 to 31.59±0.00, 0.87±0.00 to 2.22±0.00, 2.34±0.00 to 5.00± 0.00 and 1.06±0.00 to 1.45±0.00 respectively. Concentration of Fe was significantly higher than other heavy metals in the five study areas.

Table 3: Shows Heavy Metal Concentrations in Soil Samples for the wet season (mg/kg)

Sampling sites	Fe	Cu	Zn	Cd
Karu	546.28±0.01	0.65 ±0.00	12.65±0.00	0.16 ±0.00
Kugbo	534.41±0.01	1.68± 0.00	15.76±0.01	0.10 ±0.00
Nyanya	543.47±0.01	0.35± 0.00	6.19 ±0.01	0.13 ±0.00
Apo	534.41±0.00	0.54 ±0.00	32.06±0.00	0.29 ±0.00
Lugbe	549.28±0.01	0.76 ±0.00	7.2 ±0.00	0.07 ±0.00
Control	169.85±0.01	0.10 ±0.00	4.10 ±0.00	0.01 ±0.00

Mn	Ni	Pb	Cr
10.25 ±0.01	1.24 ±0.01	4.69±0.02	1.29 ±0.00
31.59 ±0.00	0.87 ±0.00	5.00±0.00	1.14 ±0.00
11.26 ±0.00	2.22 ±0.00	3.53±0.00	1.06 ±0.00
11.48 ±0.01	2.13 ±0.01	3.07±0.00	1.45 ±0.00
9.90 ±0.00	1.44 ±0.00	2.34±0.00	1.06 ±0.00
3.64 ±0.00	0.80 ±0.00	1.89±0.00	0.99 ±0.00

Table 4: Shows the seasonal variations in the concentration in the mean levels of heavy metals in soil samples. The trend among metals in wet season was Fe > Mn > Zn > Pb > Ni > Cr > Cu > Cd while it was Fe > Mn > Zn > Pb >Cr > Ni > Cu > Cd in dry season.

Table 4: Shows Seasonal Variations in the Mean Levels of Heavy Metals in Soil (mg/kg)

	Season	
Heavy Metals	**Wet**	**Dry**
Fe	541.57 ± 6.85	673.83 ± 12.87
Cu	0.80 ± 0.52	1.58 ± 0.87
Zn	14.77 ± 10.43	20.17 ± 9.56
Cd	0.15 ± 0.09	0.41 ± 0.11
Mn	14.90 ± 9.36	20.61 ± 5.73
Ni	1.58 ± 0.58	2.85 ± 0.46
Pb	3.73 ± 1.11	7.45 ± 3.80
Cr	1.2 ± 1.70	3.35 ± 1.29

Table 5: Shows WHO Permissible Limits for Heavy Metals in Soil (mg/kg)

Elements	Target value
Cd	0.8
Zn	50
Cu	36
Cr	100
Pb	85
Ni	35

IV. Discussions

Physicochemical parameters of soil samples

The pH of the soils from Karu, Kugbo, Apo and Lugbe sites were acidic in dry season that of Nyanya site was slightly acidic in wet season while the control site is neutral in wet and dry season. Soil pH was more acidic in dry season than in wet season, this may be as a result of rainfall that dilutes the soil solution leading to pH increase. At low pH, metals are more soluble in the soil solution, and more bioavailable to plants. Therefore, toxicity problems are more associated with acidic soils than in alkaline soils. The pH of the soil samples were in the same range as the values reported for seasonal variations in heavy metal concentrations in soil and some selected crops at a landfill[14], lower than the 6.3 to 7.1 reported for seasonal variations of heavy metals concentration in abattoir dumping site soil[15].

Cation exchange capacities of the soil samples values in the dry season were higher than that of the wet season. CEC can regulate the mobility of metals in soils and increases as pH increases. The values obtained were slightly higher than that reported for the evaluation of heavy metals in soils around automobile workshop clusters in Gboko and Makurdi[16], however, it is similar with some of the values reported on the impact of Nigerian flood disaster on the soil quality of farmlands[17].

Organic matter contents were higher in the study areas than that of the control which may be due to the presence of more waste from the activities carried out around the sites, there was slight difference in the contents of control soil in both seasons. Organic matter values were higher in wet season than in dry season, this may be attributed to increase in moisture content[18]. The organic matter plays important role in metal complexation. The range of organic matter values obtained in this study is in agreement with that reported for soil pollution in two auto-mechanic villages in Benin City[4].

EC measures the electrical conductivities of the water-extracted from soils which is an indication of the relative water-soluble salt contents of the soil. It depends on the amount of dissolved minerals and gives the ability of a substance to conduct an electric current at a specific temperature, usually (25 ^{0}C)[19]. The range of EC values obtained in this study were lower than 108 to 201 µS/cm values reported for soil samples around metal scrap dump in some parts of Delta State[20].

Heavy Metal Concentrations in Soils

Values of iron (Fe) obtained from the study areas were far lower than the values reported for Levels of Pb, Fe, Cd and Co in soils of automobile workshop in Osun State, Nigeria[14, 15, 21], but higher than the values reported for heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis and the Impact of Nigerian flood disaster on the soil quality of farmlands respectively[22,17]. Iron had the highest concentrations in all the sites. This is because it has been reported that natural soils contain significant concentration of iron[17]. Other things that may contribute to the high concentrations include wastes generated in these study areas which includes solvent, hydraulic fluid, spent lubricants most of which are dumped directly into the soil for so many years.

Copper (Cu) values were higher than that of the control site. The concentrations obtained in this study were all below 36mg/kg WHO[1]. Values obtained were within the range reported by[22,23,17], but lower than the values reported for heavy metals in soils around auto mechanic workshop clusters in Gboko and Makurdi, North Central Nigeria[14,15,16]. The presence of copper in the soil of the study areas could be as a result of mechanic wastes containing electrical and electronic parts, such as copper wires, electrodes and copper pipes and alloys from corroding vehicle scraps which have been deposited on the soils for a long time.

Zinc (Zn) concentrations obtained from the soil samples were all below 50mg/kg[1]standard. Similar levels have been reported for heavy metals concentration in soil and *Amaranthus retroflexus* grown on irrigated farmlands in the Makera Area, Kaduna[24]. These values were however, lower than the values reported by [14,4], but higher than values reported for heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis [12]. Presence of zinc in the soil could be as a result of elements from the lubricating oils and metal scraps from vehicles.

Concentration of cadmium (Cd) obtained from these study areas were below WHO[1] permissible limit of (0.8mg/kg). Values obtained were similar to those reported for heavy metals in soils of auto mechanic shops and refuse dumpsites in Markurdi, Nigeria[25]. These levels were however, lower than the results reported by[14,16],

but higher than values reported[24]. The presence of cadmium could be due to the dumping of Poly vinyl chloride (PVC) plastics, nickel-cadmium batteries, motor oil, vehicle wheel and disposal sludge in the auto-mechanic shops[8].

Manganese (Mn) values obtained were within the range reported by[17], but lower than the values reported by[14,15,16], Manganese is among the most abundant element in the earth's crusts and is widely distributed in soils, sediments, rocks and water. Although manganese is a component of subsoil material in form of oxide, its presence can also be attributed to discard used batteries, metal rails, machinery parts and wastes from welding works, which might have been transported and deposited by the flood[17].

Nickel (Ni) concentrations obtained were all below 35 mg/kg WHO[1] standard, showing that, there was little anthropogenic contribution. Similar levels have been reported by[4], these levels, however, were lower than the concentration reported by[14,15,16], but slightly higher than values reported for heavy metal concentrations in soils around dump sites in lafia metropolis, Nasarawa state[22]. Nickel contamination could be as a result of disposal of spent automobile batteries and different paint wastes directly on the soil.

Lead (Pb) concentrations obtained were below 85mg/kg WHO standard. The levels were in agreement with that reported by[4], however, much lower than the concentration reported by [15,16,21], but higher than the values reported by[17,22]. Lead concentration may have resulted from lead containing compounds being used in the automobile workshops.

Chromium (Cr) concentrations obtained from the soil samples were below 100 mg/kg. The levels are in accordance with that reported by[14], these levels were much lower than the values reported by[14,15], but a little higher than values reported for the impact of Nigerian flood disaster on the soil quality of farmlands[17]. The major source of chromium is from chromium containing wastes, especially industrial effluents. Chromium is commonly found at contaminated sites in form of chromium (VI) and it is the dominant form of chromium in shallow aquifers where aerobic conditions exist[17].

Seasonal variations in the mean levels of heavy metals in soil (Table 4) revealed that the mean levels were higher in dry season than in wet season. Iron has the highest value while cadmium has the lowest value.

V. Conclusion

The soil samples collected from the automobile workshops in rainy and dry seasons showed that the heavy metals analyzed were present in considerable amounts when compared with their corresponding control samples and this suggests soil contamination, the values of the heavy metal concentrations obtained in the soil samples were within WHO permissible limits. Generally higher heavy metal concentrations were recorded in soils during the dry season than in the wet season, and in these seasons, the soils were polluted mainly with iron, zinc and lead. Fe had the highest values in dry and wet seasons, while cadmium had the lowest values in both seasons.

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