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Original Research Article

Delineation of heavy metals in soils from auto-mechanic workshops within Okitipupa, Ondo State, Nigeria

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Auto Mechanic Workshops in the study area generate waste containing hazardous, soil samples were collected from selected automobile workshops (four) in the study area at the depths of 0-15cm, 30-45cm, 45-60cm, 60-75cm and 75-100cm. A total of twenty- four (24) soil samples were collected in four different locations in the ancient town of Okitipupa. Six control samples were also collected in a farm land about 3km away from Auto Mechanic Activities. The soils were analysed for heavy metals levels. Ten heavy metals (Cd, Zn, Cu, Cr, Pb, Fe, Mn, Co, Ni and Mg) were analysed using AAS techniques. The heavy metal concentration for the ten metals determined in soil was in the order; Fe > Mg > Zn >Mn> Cu >Pb> Ni > Cr > Cd > Co. Heavy metals concentrations (mg/Kg) Ranging from 0.01±0.00 to 112.00±0.00 in all the sites. Site C is about ten years older than others recorded the highest concentrations of heavy metals in all the sites. Comparing the results of the study area with the control shows that the study area is moderately contaminated; the values obtained were below the DPR permissible limit for soil. It is therefore recommended that a separate portion of land be set apart for automobile workshops in Okitipupa.

Key words: Heavy metal, soil, pollution, automobile, profile, contamination plume.

INTRODUCTION

Waste generation in the auto mobile workshop environment as a result of artisan activities includes metal scraps, used batteries, packaging materials, spent lubricants and worn-out parts, which contain contaminants such as heavy metals (Pam et al*.,* 2013a; Pam et al*.,* 2013b). Where such activities are not properly monitored and regulated, they may give rise to elevated levels of metals and hydrocarbons in the environment. Soil being a universal receptor; contain large amounts of heavy metals and hydrocarbons with varying concentration ranges depending on sources, both natural and anthropogenic. Heavy metal refers to any chemical element that has relatively high density, thus at least five (5) times the specific gravity of water (Oguntimehin and Ipinmoroti, 2008). Some metals such as manganese, iron, zinc, selenium, cobalt, copper etc. are nutritionally important for healthy life and major biochemical processes, while most of them are deleterious even at trace amounts. Examples of such as arsenic, lead, cadmium, mercury, nickel etc. Human's exposure to heavy metals is through two main absorption pathways; inhalation and ingestion (Islam et al., 2007). Complete avoidance of exposure to the toxic metals is completely impossible (Singh, 2011), metal toxicity risk can be reduced through lifestyle choices that limit the potential of heavy metal uptake (Peraza et al., 1998).

Within the European community the eleven elements of highest concern are arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin, and thallium, the emissions of which are regulated in waste incinerators. Some of these elements are actually necessary for humans nutritional benefits at moderate concentrations (cobalt, copper, chromium, manganese, nickel) while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth (nickel, cadmium, copper, chromium).

Heavy metals contaminate the soil from different sources and show different behaviour in soil (Soltan et al., 2012). According to (Dube et al., 2001), the ability of soil to immobilise introduced chemicals like heavy metals depends on sorption properties of the soil (soil texture, pH, moisture content and cation exchange capacity). Metals on the surface of the soil may be carried by runoff water and transported to the groundwater (Wuana and Okieimen, 2011).

Other heavy metal pollution sources apart from automobile workshop environments are purification of metals, e.g., the smelting of copper and the preparation of nuclear fuels. Electroplating is the primary source of chromium and cadmium. Cadmium, lead and zinc are released in tiny particulates as dust from rubber tires on road surfaces; the small size allows these toxic metals to rise on the wind to be inhaled, or transported onto topsoil or edible plants (Charles, 1997). Through precipitation of their compounds or by ion exchange into soils and muds, heavy metal pollutants can localize and lay dormant, which can have severe effects on the environment. Unlike organic pollutants, heavy metals do not decay and thus pose different kinds of challenge for remediation. Plants, mushrooms, or microorganisms are occasionally successfully used to remove some heavy metals such as mercury. (Raskin and Ensley, 2000). This study was therefore aimed at assessing the extent of heavy metal contamination in soils due to auto mechanic activities within Okitipupa Metropolis, study the distribution of the metals at different depth of the soil profile, analyse factors of distribution evaluate correlativity between metals in the samples and control and to apportion natural or anthropogenic sources, develop a 3D pictorial view of the soil and analyse its environmental significance.

MATERIALS AND METHODS

Study area

Okitipupa, Ondo –State, Nigeria was chosen for the present study. It is situated between 6° 30' 0" North, 4° 48' 0" East. It has an area of 803 km^2 and a population of 233,565 at the 2006 census. It is the single largest industrial cluster involving artisans in Ikale land. Figure 1 is the map of Okitipupa showing the sampling points.

Soil sampling

A total of twenty four (24) composite soil samples were collected from four (4) selected automobile workshops within Okitipupa using standard soil auger, at the depths of 0-15 cm, 15-30 cm, 30-45 cm, 45-60 cm, 60-75 cm and 75-100cm representing six samples per location, respectively. Soil samples were collected at random from the five different locations at each automobile workshop which were then mixed up to obtain a composite soil sample at each soil depth separately. The soil samples were placed in polythene bags and transported to the laboratory. The location and elevation of each selected site was recorded with a global positioning system (GPS, Magellan Explorist210) The six (6) control samples were collected from the Ondo State University of Science and Technology (OSUSTECH),Farmland (about 3km away from the point of impact) where there are neither car repairs nor commercial activities, with no drainage influence.

Soil sample treatment and analysis

Soil samples were air-dried at room temperature for 1 week to avoid microbial degradation. The samples were homogenized and gently crushed repeatedly using a mortar and pestle, and passed through a 0.125mm sieve prior to analysis. 1g of a well homogenized sample obtained from sample preparation procedure above was weighed into a standard Erlenmeyer flask and 12mL of freshly prepared aqua regia (HNO_3:HCl, 1:3) was added. The beaker was covered and the contents heated for 2 hrs on the medium heat of a hot plate. The mixture was allowed to cool and then filtered through a Whatman No. 42 filter paper into a 50mL standard volumetric flask. The filtrate was diluted to 50mL with de-ionized distilled water (Ehi-Eromosele et al., 2012). Blank solutions were also prepared using aqua regia and de-ionized water. The digested sample solution were analysed using the atomic absorption spectrometer {Buck Scientific 210 VGP Atomic absorption spectrophotometer, (AAS)}. Standard solutions of the various heavy metals were analysed. All soil samples were analysed in triplicate to minimize error.

Statistical analysis

Statistical analysis is very useful in providing knowledge and assisting in the interpretation of data. It is widely applied in recent times to investigate the heavy metal concentration, accumulation and the distribution in soils (Qishlaqi and Moore, 2007). Statistical analyses of heavy metal contents in soil samples from Auto mechanic Workshops in Okitipupa were performed using one way Anova to estimate the mean value, standard deviation and standard error analysis by the software package SPSS version 16.0.

RESULTS

The concentrations of heavy metals in soils from all the sites are shown on Table 1. All the metals investigated in the present study were detected in all the sites but not in all the samples. The metals concentrations were not generally high at the top soils. This is in contrary to the results of (Osakwe and Okolie, 2015) this may be as a result of seasonal variation in time of sampling. The samples in this research were collected around September when the rainfall was at the peak, other factors such as high percentage sand composition and low pH values as

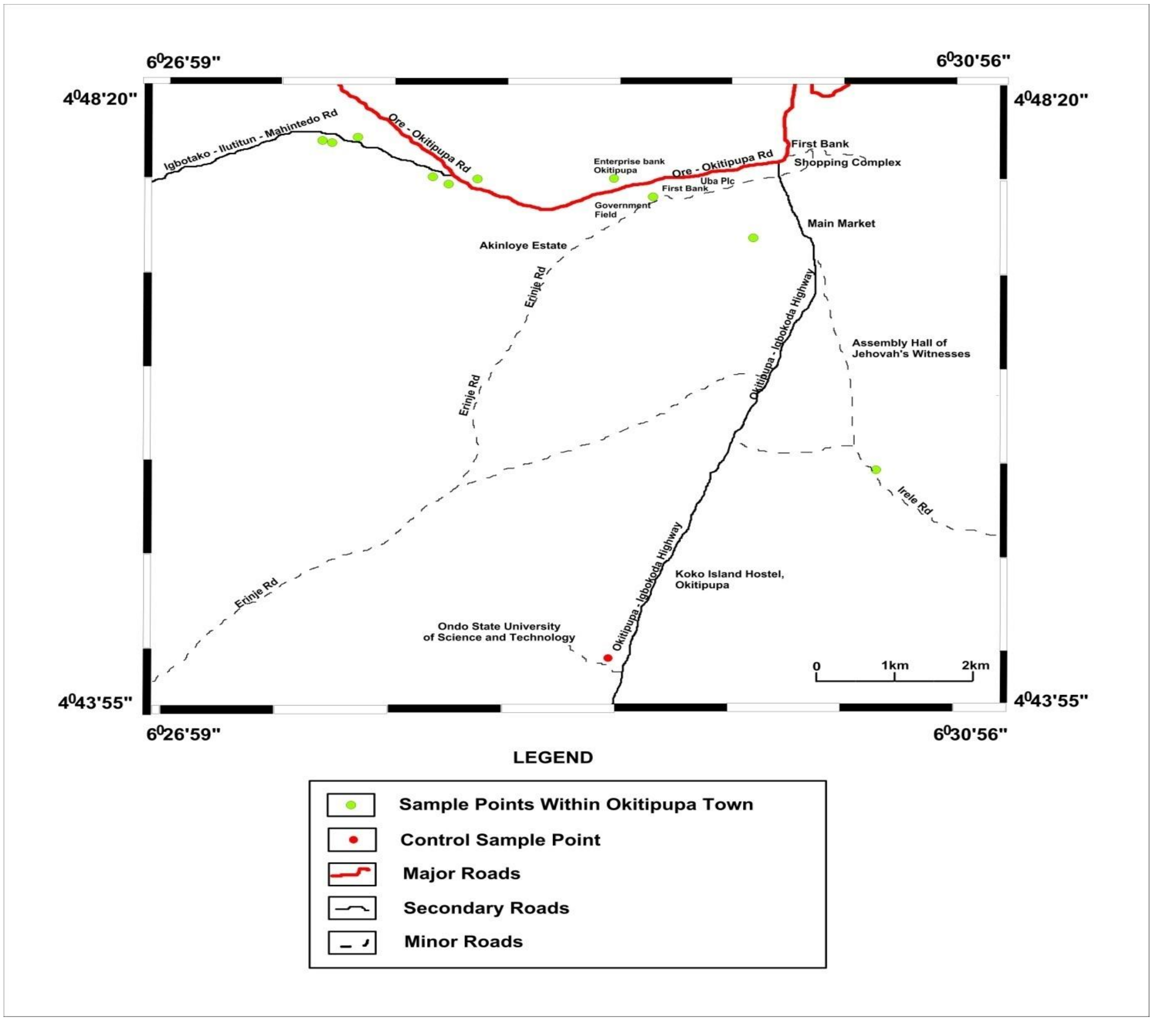

Figure 1: Map of Okitipupa showing the sampling points

Table 1. Maximum Allowable Limit (MAL) and Target Values (mg/Kg) for Heavy Metals in Soils with the Highest Values Obtained in Okitipupa

Heavy Metals	Australia [a]	Canada [a]	Poland [a]	Japan [a]	G. Britain [a]	Germany [a]	Nigeria [b]	Okitipupa[c]
Cd	5	8	3	-	3	2	0.8	0.12
Co	50	25	50	50	-	-	20	0.12
Cr	100	75	100	-	50	200	100	0.42
Cu	100	100	100	125	100	50	36	1.00
Ni	100	100	100	100	50	100	35	0.21
Pb	100	200	100	400	100	500	85	0.8
Zn	300	400	300	250	300	30	140	1.76
Fe	-	-	-	-	-	-	-	112
Mg	-	-	-	-	-	-	-	7.01
Mn	-	-	-	-	-	-	-	0.95

Values for a Standard soil 10% organic

reported in the previous work by the authors in those sites may be responsible for the solubility and mobility of the metals (Adebayo et al., 2016). The metals levels in most of the sites were significantly higher than the levels observed

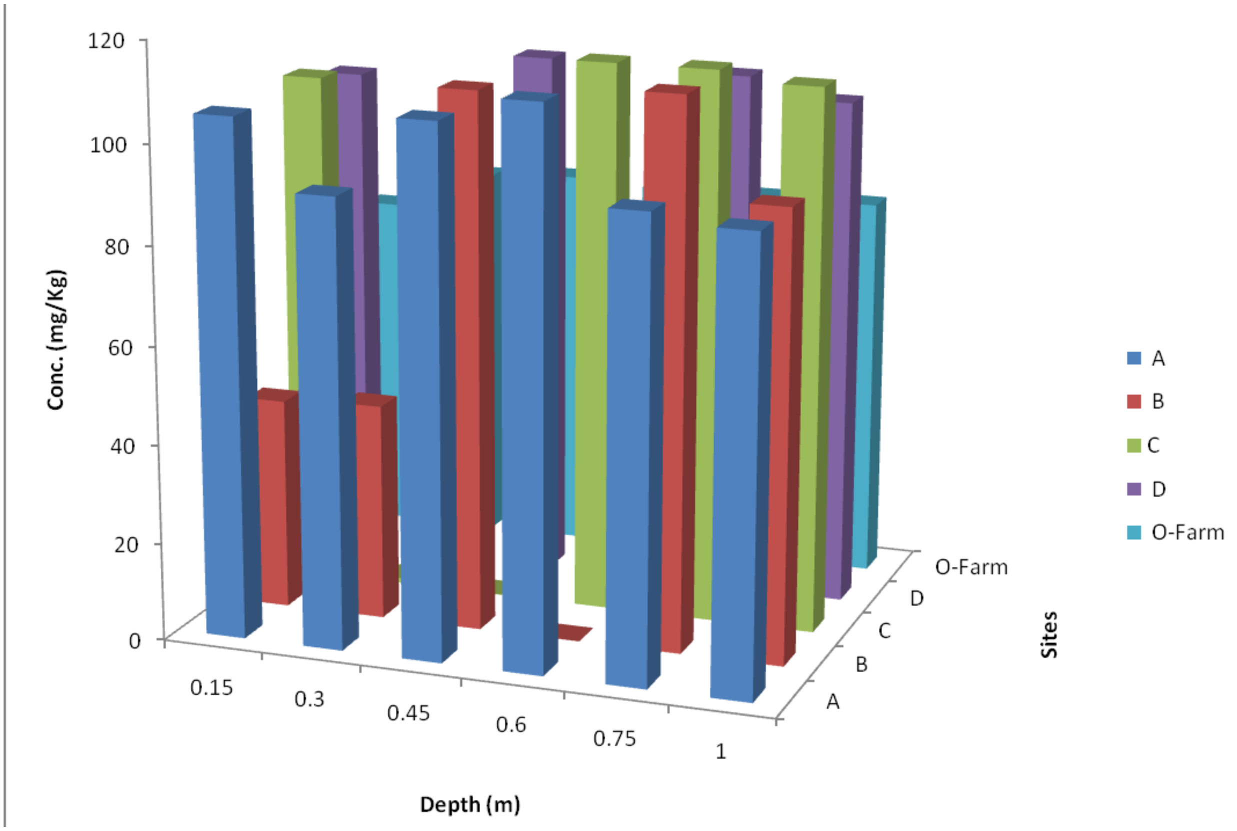

Figure 2: Fe Conc.(mg/Kg in all the sites and control

in the control sites. This shows that metals accumulations in the samples is more of anthropogenic than natural sources. Figure 2- 11 Show the 3D pictorial View of the heavy metals studied in all the sites

DISCUSSIONS

Fe has the highest mean concentration among all the metals studied and its concentrations ranged from 0.15 to 112mg/kg. High concentrations of iron in soils relative to other metals have been reported in various studies, confirming that natural soils contain significant levels of iron (Dara, 1993; Ademoroti, 1996; Aluko Oluwande, 2003; Oguntimehin and Ipinmoroti, 2008). The mean value of iron obtained in this study is similar to those obtained by Osakwe, 2014 but lower than those reported by Oguntimehin and Ipinmoroti, 2008; Osakwe, 2010; Nwachukwu et al., 2011; Idugboe et al., 2014. It is also higher than the values reported by Okorie and Egila 2012, Agbogidi, 2013,Suleman, 2014.The highest concentration of iron was present in soil samples from the Site C (oldest) and Site A. High values may be attributed to rust of old vehicles bodies, welding and panel beating activities on the site. Figure 2 is a 3-D pictorial view of Fe concentrations in all the sample sites and the control. Generally high concentrations of Fe were found to be accumulated between the depth of 0.45m and 0.75m. 112mg/Kg of Fe was found to be at Site C depth 0.6m to 0.75m and Site A at depth 0.6m where the pH values were found to be minimum (highest acidity). Low concentration of Fe in human leads to anaemia. Acute exposure of Fe in human leads to vomiting cardiac depression and metabolic acidosis Soghoian, 2011.

Zinc concentrations in samples (mg/kg) vary from 0.07-1.76 and control with the range 0.25- 1.04. The range of values obtained in this study is lower than those reported by Oguntimehin and Ipinmoroti, 2008;Iwegbue et al., 2013; Zakir et al., 2014; Oswakwe, 2014; and Ojo et al., 2015 but higher than the levels reported by Nwachukwu et al., 2013; Ubwa et al., 2013. The highest concentrations of Zn were obtained in Site C at depth 0.15. The high level of zinc in Site C could be attributed to the age of the site which is about twenty four years and also as a result of its location along the roadside. Roadside soil could be attributed to the wear and tear of vehicle bodies with galvanized steel surfaces (Zakir et al., 2014). Zinc is used in brake linings of vehicles because of its heat conducting properties and can be released during mechanical abrasion of vehicles and from combustion of engine oil and also from vehicle tyres (El-Gamal, 2000; Akbar et al., 2006; Manno et al., 2006; Matthews–Amune and Kakulu, 2013.

Elik, 2003 reported that high concentration of Zinc in heavy traffic zones indicate that fragmentation of car tyres

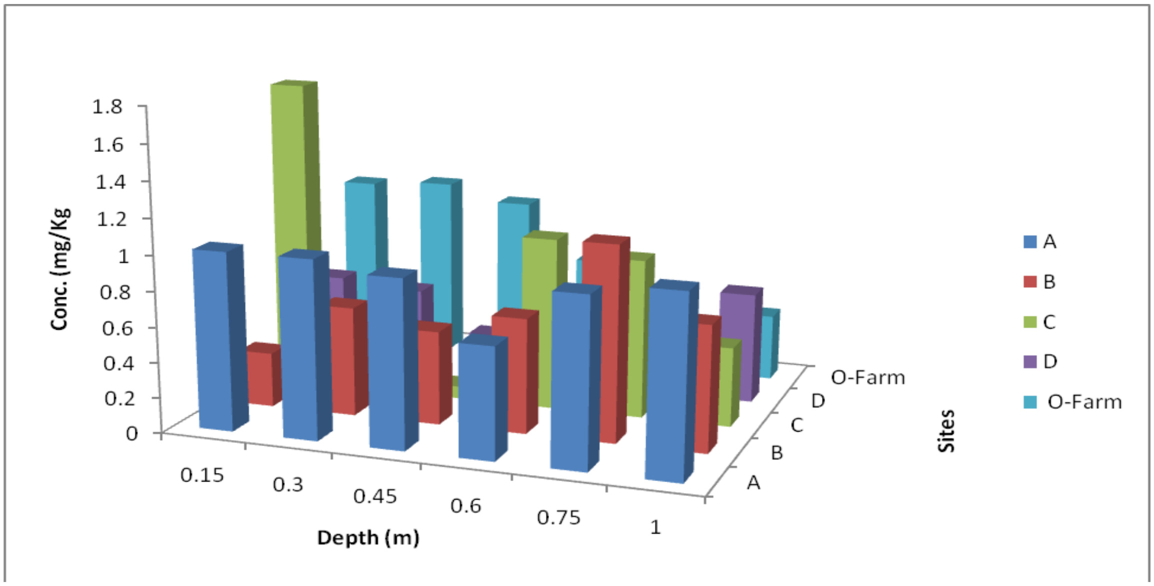

Figure 3: Zn Concentration (mg/Kg) in all the sites and control

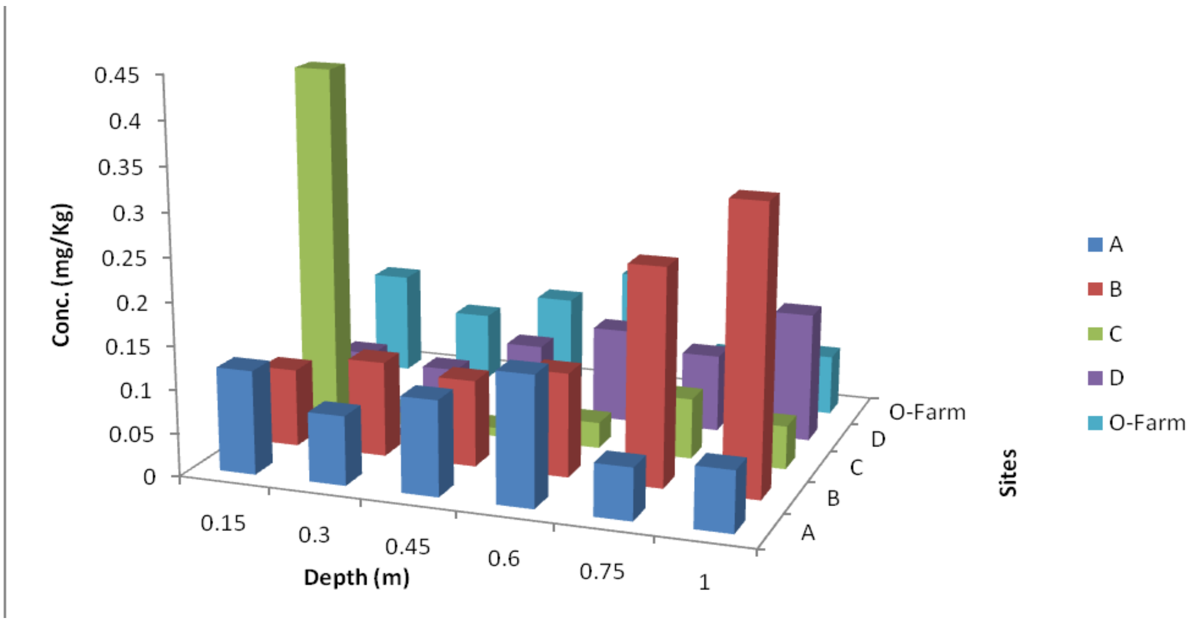

Figure 4: Cr concentration (mg/Kg) in all the sites and control

is a likely sources of the metal. Other possible sources of zinc in relation to automobile traffic in addition to wearing of brake lining are losses of oil and cooling liquid of vehicles and wearing of road paved surface (Saeedi et al., 2009). The amount of zinc recorded at Ore junction along Ikoya road was the highest probably because of the access road leading to many Ikale towns and many vehicles move to and fro from the towns to the expressway. Figure 3 below show the 3D pictorial view of Zn in all the sample locations and the control

Chromium concentrations ranged from (mg/kg) 0.01 to0.42. And was found to be highest in Site C at the depth of 0.15mthis may be attributed to the age and the location of the site which is along Ikoya road at the Ore junction of the road. Value obtained are lower than those reported by (Okoye and Egila, 2012; Iwegbue et al., 2013; Ubwa et al., 2013, Idugbose et al., 2014; Ferronato et al., 2013; Zakir et al., 2014). According to Al-Rhashman (2007), chromium level in road side soil is associated with the chromic plating of some vehicle parts used for preservation of corrosion. Chromium is carcinogenic resulting in cancer of respiratory organs in workers exposed to chromium containing dust (Langard, 1980). Figure 4 below shows the 3D pictorial view of concentrations of Cr in all the sample sites and the

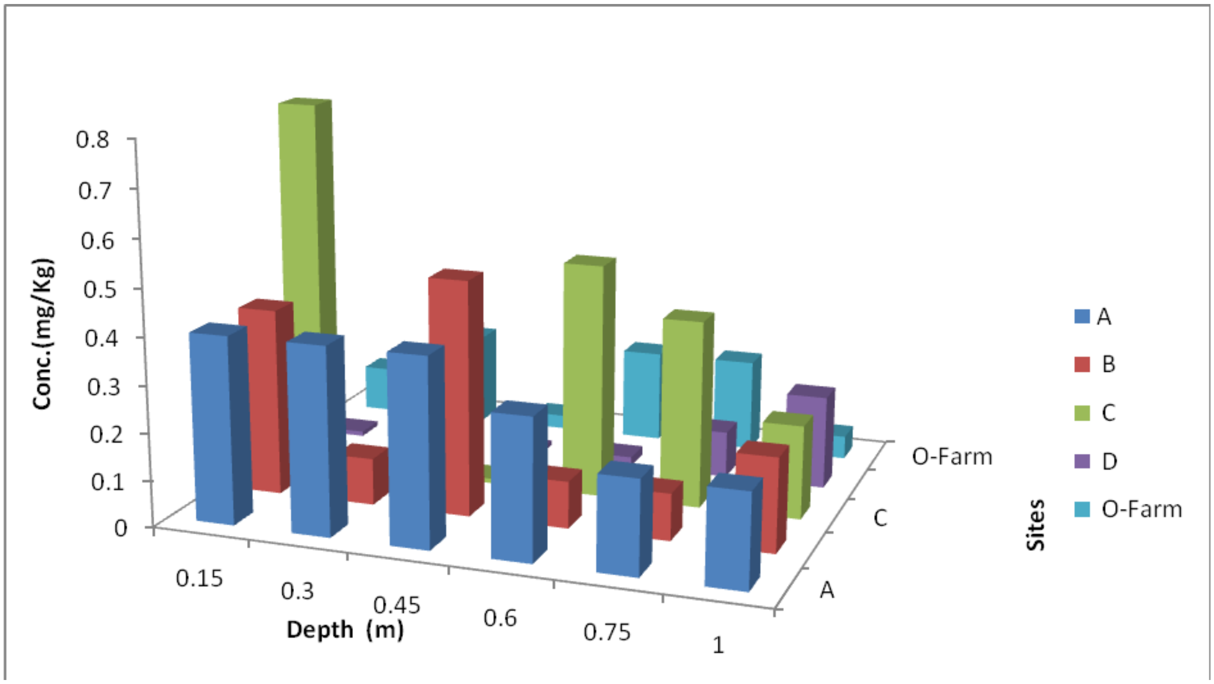

Figure 5: Pb concentration (mg/Kg) in all the sites and control

Control.

Lead Concentrations in all the sample sites were in the range of (mg/kg) 0.01 to 0.80Thisrange of values for lead was lower than those reported by Zakir, et al., (2014); Das et al; (2015). However the lead levels observed in this study are significantly higher than those reported by Matthews-Amune (2013), Ubwa et al., (2013) and lower than those of other similar studies (Nwachukwu et al., 2011; Najib et al., 2012; Pam et al., 2013). The concentration of lead in the soil is likely to have derived from vehicle exhaust fumes containing some lead-rich aerosols. (Zakir et al., 2014). Studies have shown that the use of tetraethyl lead as an antiknocking agent in gasoline gives rise to its release during emissions from automobiles and fossil fuel combustion (Oztas and Ata, 2002, Akbar et al., 2006, Onder et al, 2007, Sharma and Parasade, 2010). Sherene (2010) reported that major sources of lead pollution are exhaust gases of petrol engines, which account for nearly 80% of the total lead in the air Kakulu, (2003) also reported that lead content of leaded gasoline in Nigeria ranges from 0.60 to 0.80g/l. In addition, lead levels in roadside can also be attributed to wearing down of vehicle brake linings and tyres (Sharma and Prasade 2010, Zhang et al., 2012), Soerme and Langerkvsith, 2002). Elevated levels of lead constitute serious health risk. Purefoy, (2010). Figure 5 shows the 3-D pictorial view of concentration of Pb in the sample sites and the Control. Site C at depth 0.15m has the highest concentration of lead in all the sites.

Nickel concentrations in the soils from all the sites ranged from (mg/kg) 0.01 to 0.21. The highest value of nickel obtained in this study is lower than values reported by Najeb et al., 2012; Ogundiran and Osibanjo, 2009; Oguntimehin and Ipinmoroti, 2007; Nwachukwu et al., 2013. The highest value of nickel obtained in this study is however higher than that reported by Pam, et al., 2013; Matthews – Amune and Kakulu, 2013; Ubwa et al., 2013. Airborne particles emitted by brakes and wears from vehicle tyres can contain considerable amounts of nickel (Onder et al., 2007). This is a probable source of nickel in the recorded soils. Anthropogenic input of nickel in the study areas could also be from the diesel used in the automobiles (Iwegbue, 2013). Figure 6 shows the 3D pictorial view of Ni in all the sites and Control. From the figure, Ni was detected in all the samples and control except at depth 0.6m of the control. The highest concentration of Ni (0.21 mg/Kg) was obtained at site C depth 0.15m. Exposure to intake of large amount of nickel from plants, grown on nickel rich soil leads to higher chances of developing cancer of the lungs, nose, larynx and prostrate as well as respiratory failures, birth defects and heart disorders (Duda-Chodale and Blaszezyk, 2008; Lentech, 2009). The concentrations of Ni obtained in this work are below the DPR permissible limit of Ni in the soil.

Manganese concentrations ranged from 0.12 to 0.95(mg/Kg). Mn levels obtained in this study are relatively lower than the values reported by Eddy et al., 2003. Although the concentration found for Mn is above the control level, there is, at present, no soil quality criteria established for Mn. Nevertheless, Mn in the soils examined need to be further monitored to prevent an explosive increase.

Potential sources of Mn could be from used batteries,

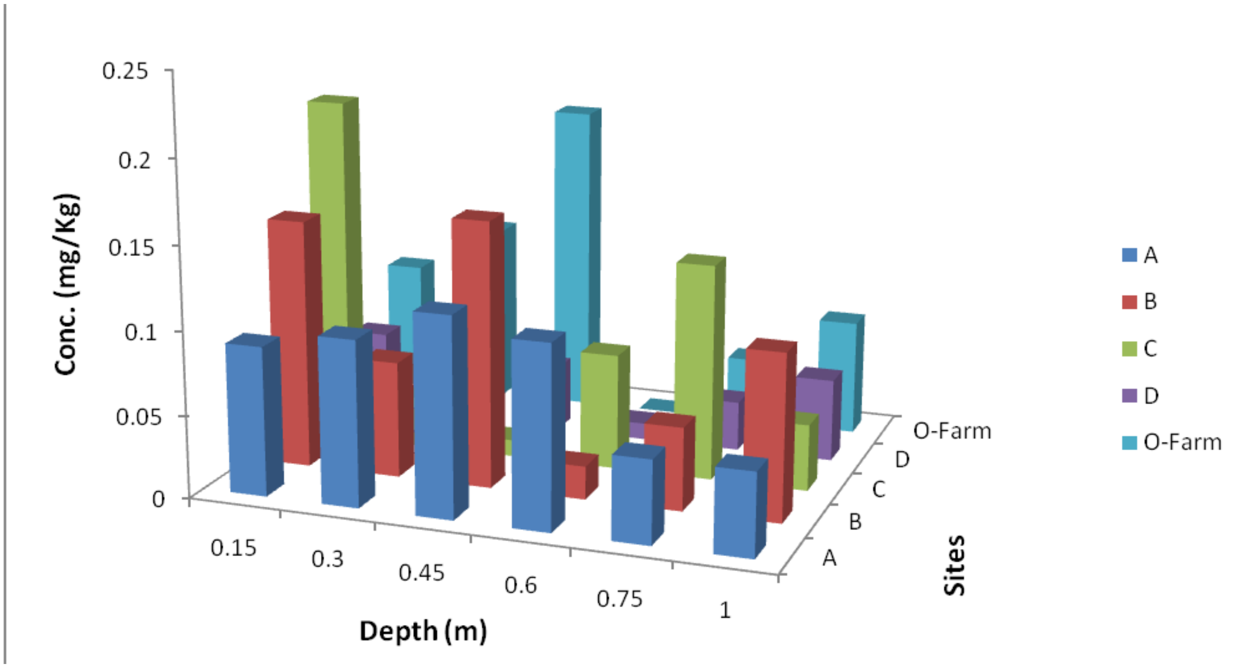

Figure 6: Ni concentration(mg/Kg) in all the sites and control

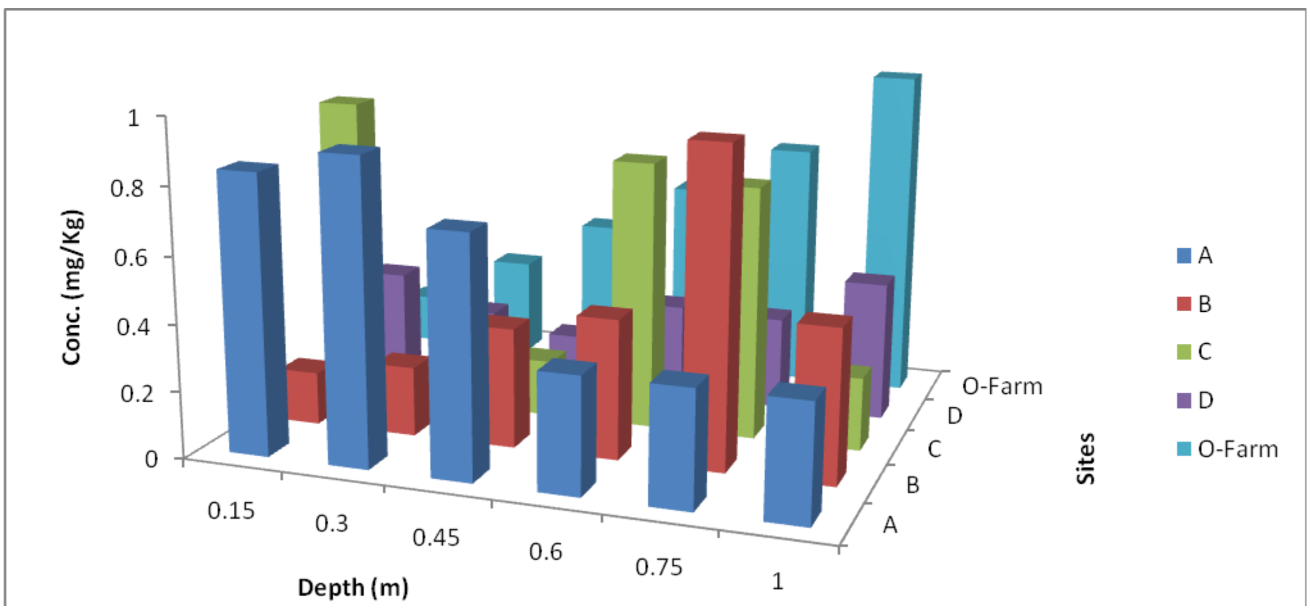

Figure 7: Mn concentration (mg/Kg) in all the sites and control

discarded metal rails, machinery parts and wastes from welding works and spray paintings of vehicles. Mn in trace amounts is an essential element for plants and animals, its optimum concentrations are very essential for respiratory enzymes and connective tissues development. High concentration of Mn results in Kidney failure, liver and pancreas malfunctioning Underwood, (1977). Exposure to abnormally high concentration of Mn particularly in form of dust and fumes is known to have resulted to adverse effect on humans Waldboh, (1978). Figure 7 shows the 3D pictorial view of Mn in all the samples sites and control. The lowest concentration was recorded at site C depth 0.3m and the highest concentration at site B depth 0.75m. Mn was detected in all the sample sites and the control.

Copper concentrations ranged from (mg/Kg) 0.01 to 1.00 similar ranges of values have been reported by Iwegbue et al., (2006), Osakwe, (2014). The values are however lower than those reported by Nnabo, et al., (2011), Okoye and Agbo, (2011), Kuar and Mehra, (2012), Ekpete and Festus, (2013) and higher than values reported by Osakwe, (2012).

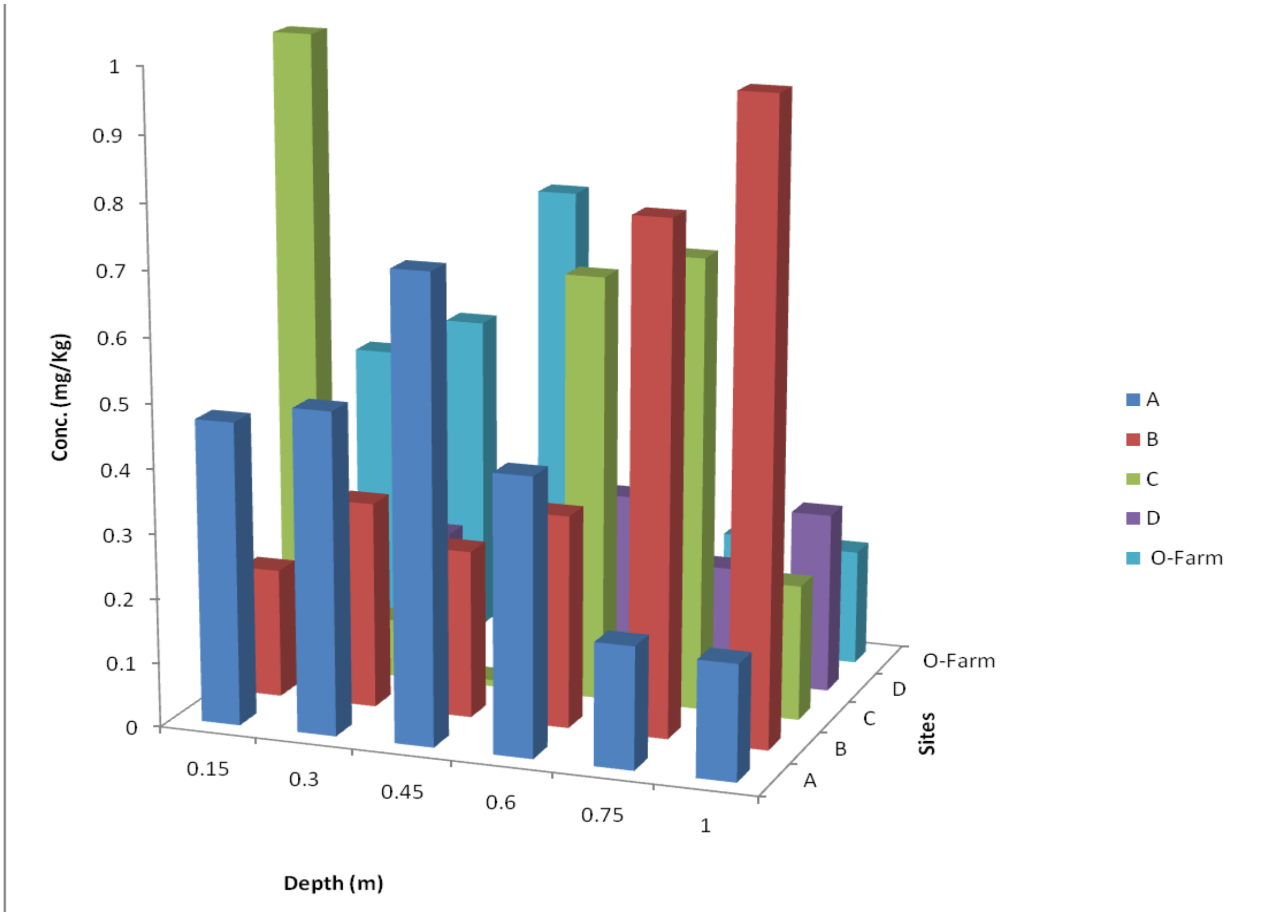

Figure 8: Cu concentration(mg/Kg) in all the sites and control

Used oils that sink into the ground as leachates contain high proportions of copper as well as lead and antimony. Metal bearing wears are also a possible source of copper. Although copper is essential for plant growth, a very small amount of copper ions cause headache, nausea, vomiting and diarrhoea and at high concentrations they cause anaemia, gastrointestinal disorder and also lead to liver and kidney malfunctioning in extreme cases USEPA,(1999). Based on DPR standard the permissible limit of Copper in soil is 36mg/Kg and maximum copper concentration in this study 1mg/kg at site C depth 0.15m. This value is far below the permissible limit for copper in the soil. Figure 8 shows the 3-D pictorial view of Copper in all the sites and the control.

Cadmium highest concentration obtained in this study is 0.12 mg/kg and ranged from 0.01 – 0.12 mg/kg. The concentrations obtained in this work is relatively low compare to criteria acceptable in most countries Lacatusu, 2002 but higher than the control values. This finding of elevated Cd concentration is consistent with that of Luter et al., 2011 which investigated heavy metals in soils of auto-mechanic shops and refuse dump-sites in Makurdi, Nigeria and reported a range of 0.6–3.5 mg/kg. The maximum Cd level observed is far below that reported in Imo, South–East Nigeria Nwachuku et al., 2010. Cd was detected in all the sample sites and control except at site C depth 0.45m, site D depths 0.15-0.3m and 0.6m. The highest concentration of Cd 0.12mg/Kg was obtained at site D depth 0.45m which is not too close to the DPR maximum permissible limit in the soil. Cadmium can enter the human body through smoking cigarettes, contaminated water due to landfills, certain foods such as shellfish, and mostly through handling the metal itself. Cadmium is a very toxic metal and needs to be handled with great caution.

Lethal doses of cadmium affect various organs in animals which includes the liver, kidney, lungs, testes, skeletal, nervous and immune system and can also results in osteomalacia and osteoporosis. Cadmium is a category 1 carcinogen, Australian Minerals & Energy Environment Foundation, 2002. Figure 9 shows the 3-D pictorial view of Cd in all the sample sites and the control.

Cobalt was equally detected in all the sites and control except site C at depth 0.45m. The control concentrations range from 0.01 to 0.05 mg/Kg and sample concentration ranges from 0.01 to 0.12 mg/Kg. The highest concentration values were obtained at Sites C with 0.12mg/Kg respectively. The values are below the DPR permissible limit of Cobalt in soil and therefore pose no environmental

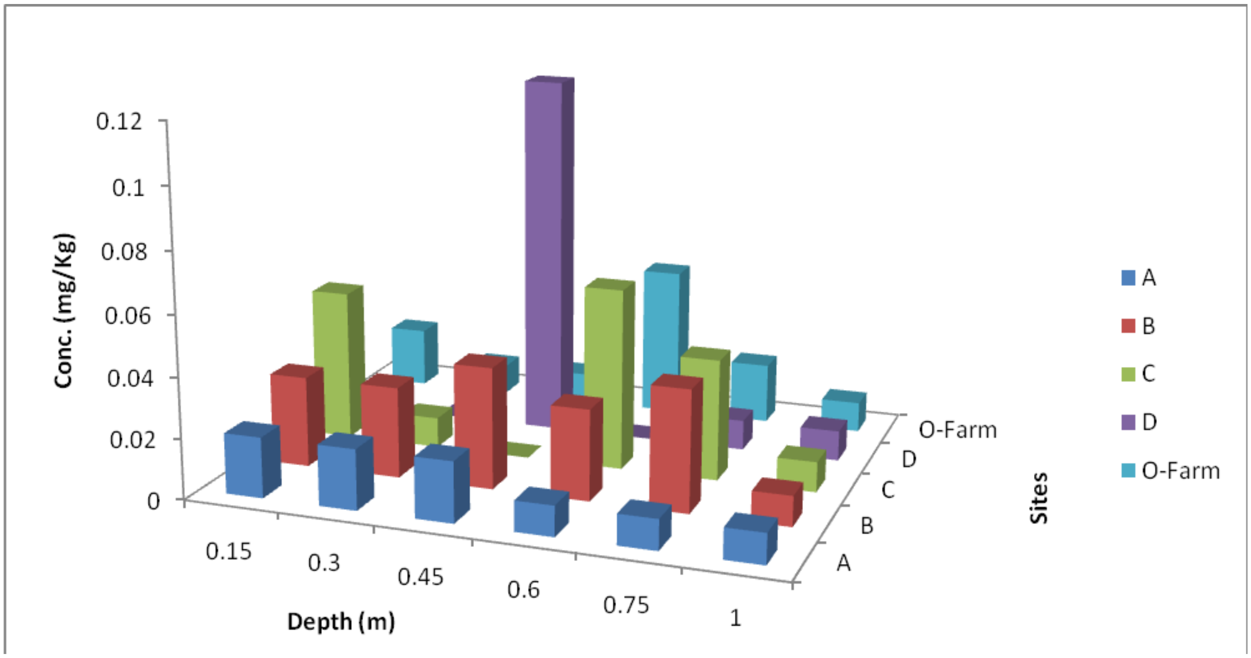

Figure 9: Cd concentration(mg/Kg) in all the sites and control

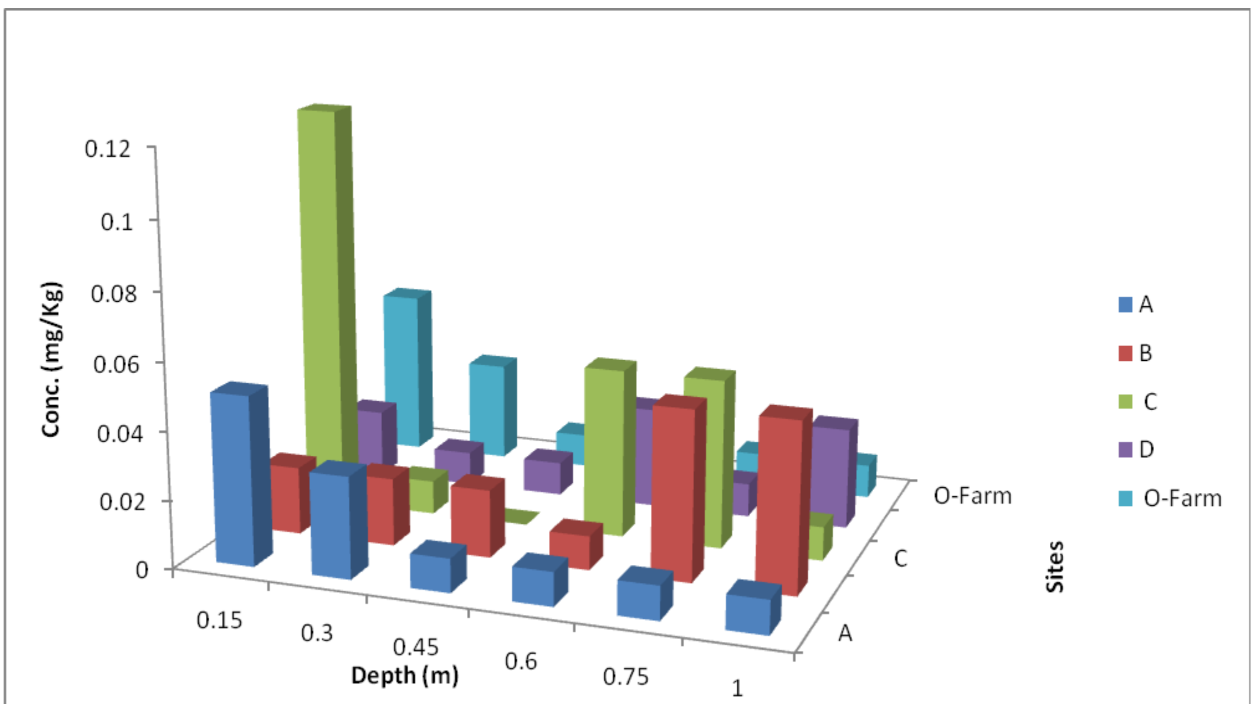

Figure 10: Concentration(mg/Kg) in all the sites and control

treat at present. Figure 10 shows the 3-D pictorial view of all the sample sites and control.

Magnesium has the second highest concentration after Iron. Mg concentrations in all the sites range from 1.41-7.01 mg/Kg and control ranges from 2.44-3.41 mg/Kg. Highest concentration of Mg is obtained at site A depth 0.75m and the least concentration at site C depth 0.45m. From the Figure 11, there are accumulations of magnesium between the depths of 0.45m to 0.75m; this may not be unconnected with high acidity around that region. Mg is not a heavy metal but was analysed to study factors responsible for its mobility. Hence its seems to pose not

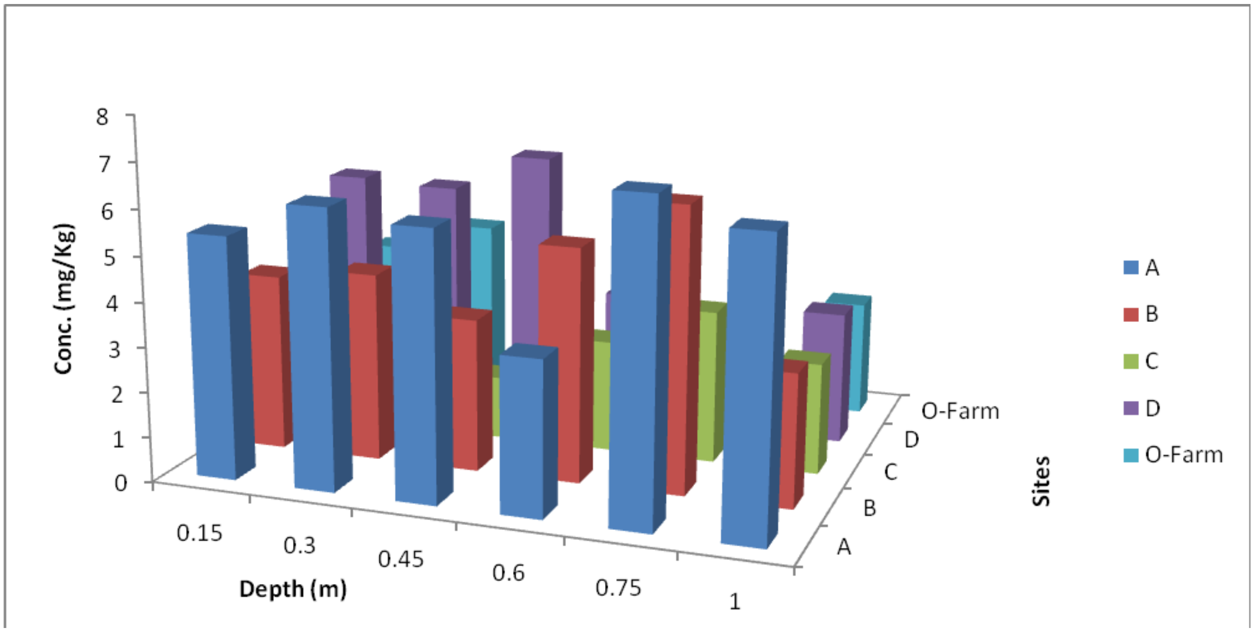

Figure 11: Mg concentration (mg/Kg) in all the sited and control

toxicity to the environment from literature search.

CONCLUSION

The heavy metal concentration for the ten metals determined is in the order and the levels of these metal; Fe > Mg > Zn >Mn> Cu >Pb> Ni > Cr > Cd > Co. The metal concentration increased with the depth of the soil profile. Auto Mechanic activities contributed to high levels of the metals .Multivariate statistical analysis such as correlation analysis was used to gain additional insight into the correlativity of these metals and their origins .The high correlation coefficients between the different metals indicate strong association between them, which probably reflects their related or common origin and contamination from auto mechanic activities, in addition to the original content from the weathered soil because these metals had mean concentrations that were higher than the control or background values.

From the study, it can be concluded that soils from the oldest and highest traffic volume sites Site C (about ten years older than other sites and have highest traffic volume) have highest level of contamination.

Acknowledgements

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Availability of data and materials

The authors declared that all the data obtained from the findings are fully availablewithout restriction.

Authors' contributions

IIO conceived and design the investigation. AAJ collected and analysed the data. AAJ prepared the first draft of the manuscript JJT, IIO and LL reviewed the final draft.

Competing interests

The authors' proclaim that they have no competing interests.

Ethics approval and consent to participate

Ethical approval was given by the Ethics Committees of the Department of Chemistry, Federal University Technology, Akure, Ondo-State. Also a written consent was also obtained from each auto workshop owner volunteer before soil samples were taken.

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