

Original Research Article

Assessment of Concentrations of Heavy Metals in Soils around ESPRO Asphalt Production and Quarry Site, Wasinmi, Osun State Southwest Nigeria

ABSTRACT

Local Government Area

This work examined the concentration of heavy metals in soil samples around a ~~quarry site~~ (ESPRO Asphalt Production and Quarry Site) located in Wasinmi, Irewole LGA, Osun State. A total of nine (9) soil samples were collected from three ~~(3)~~ points with ~~spatial variation~~ distances of 0, 1, and 2 km (0km, 1km and 2km) from the quarry site. Atomic Absorption Spectroscopy (AAS) was used to determine the concentrations of heavy metals ^{in the soil samples}. The results revealed that the mean values of the ~~assessed~~ metals ~~contents~~ in the soil samples analyzed were in the order: Fe>Zn>Cu>Cr>Mn>Pb>Cd. The concentration of the heavy metals in the soil samples were found to decrease as the soil depths ~~ranging~~ ^{increased} from 0-25cm ~~increases as well as increase in the~~ ^{and also as the} spatial ~~variation~~ ^{increased} distances of the sampled locations from the quarry plant. The study also ~~revealed~~ ^{showed that} low concentrations of Lead (Pb) ~~having~~ ^{had} a mean concentration value of 0.87ppm and Cadmium (Cd) ~~had~~ ^{with a} a mean concentration value of 0.29ppm. It was also observed that Iron (Fe) had the highest mean concentration value of 148.8ppm. The study concluded that quarrying activities raised the soil heavy metals ~~content~~ ^s up to the range of about 2km away from the quarry site. This can be attributed to the number of years of mining and excavation activities in the study area and accumulation of the heavy metal concentration ^s over time ^{and this} could be dangerous ~~for the surroundings of site~~ ^{to the site environments} especially farming and groundwater exploration ^{activities} ~~in the area.~~

Keywords: concentration, heavy metals, absorption spectroscopy, spatial variation, soil, quarrying

1. INTRODUCTION

Quarrying is necessary to provide ~~much~~ of the materials used in traditional hard flooring such as granite, limestone, marble, sandstone, slate and even ~~just~~ clay to make ceramic tiles and other application like alloying [1,3,4,11]. However, like many other man-made activities, quarrying causes a significant impact on the environment which includes air pollution, noise pollution, biodiversity damage, ^{quarry} Quarry wastes and habitat destruction. This also causes the build-up in soils of persistent toxic compounds, chemicals, salts, radioactive materials or disease-causing agents which have adverse effects on plant growth and animal health [13,18]. Due to increasing population growth, agriculture, industries and urban infrastructures in Nigeria, considerable degradation of the environment is occurring. Heavy metals are being released to the soil as a result of human activities, weathering and leaching ~~of~~ from wastes, rocks dumps to meet the everyday demand for life [5,7,15,21]. The occurrence of heavy metals in soil can be natural or as a result of human activities. The human activities include mining, smelting, domestic wastes and various industrial activities and they are the major source of soil toxin. The direct activities of extraction, processing for industrial and consumer use contributes to the mobilization of heavy metals into the soil. According to [23] and [9], ~~the situation~~ of heavy metals pollution is more worrisome in the developing countries where research efforts towards monitoring the environment have not been given the desired attention by the stakeholders. Industrial scale mining activity is comparatively low in Nigeria, yet at this level of mining, the nation is increasingly exposed to the unwanted ^{environmental} ~~ecologic~~ effects of heavy metals [2,8]. Crushed rock ^{aggregates} aggregating from quarrying generates considerable volumes of quarry dust which significantly leads to production of considerable amount of wastes harboring a number of Heavy metals [6,14,22]. Interestingly, small amount of these heavy metals are common in our environment and diet which are necessary for good health, but large amount of any of them may cause acute or

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as a result efforts being made

chronic toxicity and poisoning [10,12,16,17,19,20]. This work was designed to ^{study} determine the concentration of heavy metals in ESPRO Asphalt Production and Quarry Site ~~Company Limited~~ and assess its impact on ^{the} surrounding soil and environment. The distributions and concentration of heavy metals at varying distances (spatial variations) from the quarry site and its environment ^{as well} were ~~investigated coupled with the~~ variation of heavy metals with soil depth. ~~was~~ ^{were} studied.

2. MATERIALS AND METHODS

2.1 Sample ^Collection and Treatment

Soil Samples were taken at intervals of 0 km, 0-1 km and 1-2 km in Southeast and southwest directions of the quarry site. Two soil samples each were taken from the top layer (0-5cm) and two sub-layers of (5-10cm) and (10-25cm). Control samples were also taken in the Southeast direction where there is less pollution of heavy metals. The control samples were taken with the same parameters (distance and depth) but one sample ^{was taken at the} is obtained ~~each~~ at different points. These Soil samples were air dried and sieved using 2mm mesh size sieve to remove stones ^{and} plant roots in order to have soil of uniform particle size. The soil samples were collected in a polythene bag, ^{and placed} ~~and kept in dry place and~~ labeled appropriately until analysis. ^{and kept in dry place}

2.2 Sample Analysis

The soil samples were analyzed using Atomic Absorption Spectrophotometer, ^{1.0g or what?} (1.0 of soil) was weighed into a digestion flask, 10mL of Nitric per Chloric acid (2:1) was added to the sample and digested at 150°C for 1.5hours, 5mL of HCl distilled water (1:1) was added. The temperature was increased to 230°C and further digested for another 30minutes. It was removed from heat and allowed to cool. It was washed into a standard 100mL volumetric flask and made up to the mark with distilled water. The amount of heavy metals in the sample was determined by Atomic

Absorption Spectrophotometer (PG:990). The concentration of heavy metals was extrapolated from the calibration graph prepared.

2.3 Calculation of Metals Concentration

From the laboratory results, the elemental concentrations in parts per million (ppm) were determined by:

$$mc = \frac{c * df}{w} \quad \text{--- --- --- --- ---} \quad 1$$

where mc = Metals Concentration; c = Concentration; df = Dilution Factor; w = Weight taken

3. RESULTS AND DISCUSSION

3.1. Results

The concentration of heavy metals in soil and their spatial variation with distance in the study area is presented in Tables 1 and 2. The concentration of heavy metals in soil at a depth of 0-25cm varied with distances (0km, 1km and 2km) to the quarry site.

Table 1: Heavy Metals Contamination in Soil Samples around the Quarry Site

S/N	Sample	Distance	Depth	Concentration of heavy metals (ppm)
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No.		From the Factory (km)	(cm)	Cu ²⁺ (ppm)	Mn ²⁺ (ppm)	Fe ²⁺ (ppm)	Zn ²⁺ (ppm)	Cd ²⁺ (ppm)	Pb ⁴⁺ (ppm)	Cr ³⁺ (ppm)
1	A	0	0-5	5.20	2.44	323.2	7.35	1.50	4.43	5.23
2	B	0	5-10	4.34	1.67	275.2	7.15	1.10	3.41	3.42
3	C	0	10-25	2.36	0.83	142.6	6.36	ND	ND	1.05
4	D	1	0-5	2.10	0.81	136.4	5.44	ND	ND	0.78
5	E	1	5-10	1.23	0.80	121.5	4.26	ND	ND	0.66
6	F	1	10-25	0.97	0.79	100.4	2.25	ND	ND	0.57
7	G	2	0-5	0.86	0.76	99.4	1.05	ND	ND	0.03
8	H	2	5-10	0.75	0.60	84.5	0.25	ND	ND	ND
9	I	2	10-25	0.67	0.22	56.4	0.04	ND	ND	ND

Note: ND=Not Detected, Cd= Cadmium, Cr= Chromium, Fe= Iron, Cu= Copper, Mn= Manganese, Zn= Zinc, Pb= Lead

In the table 1, the heavy metals concentrations in the soil samples at a depth of 0-5cm ranged from 1.50ppm Cd to 323.2ppm Fe. At depth 5-10cm, the heavy metal concentrations values ranged from 1.10ppm Cd to 275.2ppm Fe, also at the depth of 10-25cm, the heavy metals concentration values ranged from 0.83ppm Mn to 142.6ppm Fe. The results revealed that as the depth increases, the heavy metals concentration values decrease and contamination occurs as a result of the quarry activities. Here, the order of contamination of the heavy metals in all depth in the quarry site with distance 0 km is Fe>Zn>Cu>Cr>Pb>Mn>Cd.

Considering the spatial variation (distance) of about 1km from the quarry site, the heavy metal concentration values in the soil sample at a depth of 0-5cm ranged from 0.81ppm Mn to 136.4ppm Fe. At 5-10cm, the heavy metal concentration values ranged from 0.66ppm Cr to 121.5ppm Fe, also the depth 10-25cm, the heavy metals ranged from 0.57ppm Cr to 100.4ppm Fe. The results obtained revealed that the trend of decreasing level of contamination was observed as the soil depth increases. The order of contamination in the heavy metals in all depth

is Fe>Zn>Cu>Mn>Cr. The heavy metals not detected are Cd and Pb. The experimental results computed in the analysis of the spatial variation (distance) of about 2km from the quarry site follows the regular pattern as the 0km and 1km distances from the quarry site. At depth 5--10cm, the heavy metal concentrations values ranged from 0.25ppm Zn to 84.5ppm Fe and also at depth 10--25cm, the heavy metal levels ranged from 0.04ppm Zn to 56.4ppm Fe. The results revealed that as the soil depth increases, the concentration of heavy metals decreases at 2km distance from the quarry site. The order of contamination of heavy metals at 2km distance from the site is Fe>Cu>Mn>Zn>Cr. Though the concentration of Cr detected was insignificant whereas Cd and Pb were not detected.

Table 2: Mean Concentrations of Heavy Metals in Soil Samples around the Quarry Site

→ Bold and Capital!

S/N	Heavy Metals	Mean Concentrations (ppm)
1	Cu	2.11
2	Mn	0.99
3	Fe	148.84
4	Zn	3.79
5	Cd	0.29
6	Pb	0.87
7	Cr	1.30

WHO Standard Limits

From Table 1, Cu decreases throughout the entire soil profile at all three locations A, B and C. It was found in highest concentration at location A (quarry site), 0--5cm depth where it reaches 5.20ppm and the lowest concentration of 2.36ppm in the sub-soil region in the location A. It can be deduced in the other two locations B and C, follow the same pattern as shown in the statistical approach which explains the decrease in the concentration of Copper as the depth of the soil samples increases. Likewise, locations A and C have the concentration of Mn decreasing with increasing soil depth while location B which is 2km away from the quarry site has relatively stable values with slight variation ranging from 0.79-0.81 ppm. Location B also follows the same pattern with depth of soil samples increasing.

Also, from the Table 1, the quarry site being the location A is highly concentrated with Fe at the topsoil (0-5cm) with a high significant concentration value of 323.2 ppm. The lowest values are present at location C which is 2km away from the quarry site. Fe decreases throughout the entire soil profile at the three (3) sampled locations. At close distances (locations B and C) from the quarry site, the soil exhibits higher Fe values than further away from the quarry site, which can be attributed to the fact that Fe concentration was found to be above 2006 WHO limits, which may be due to the deposition of quarry dusts on the soil. The effect of quarry dust pollution on

Note

Include the WHO limits of these heavy metals in soil and water in Table 2 above

World Health Organisation (WHO)

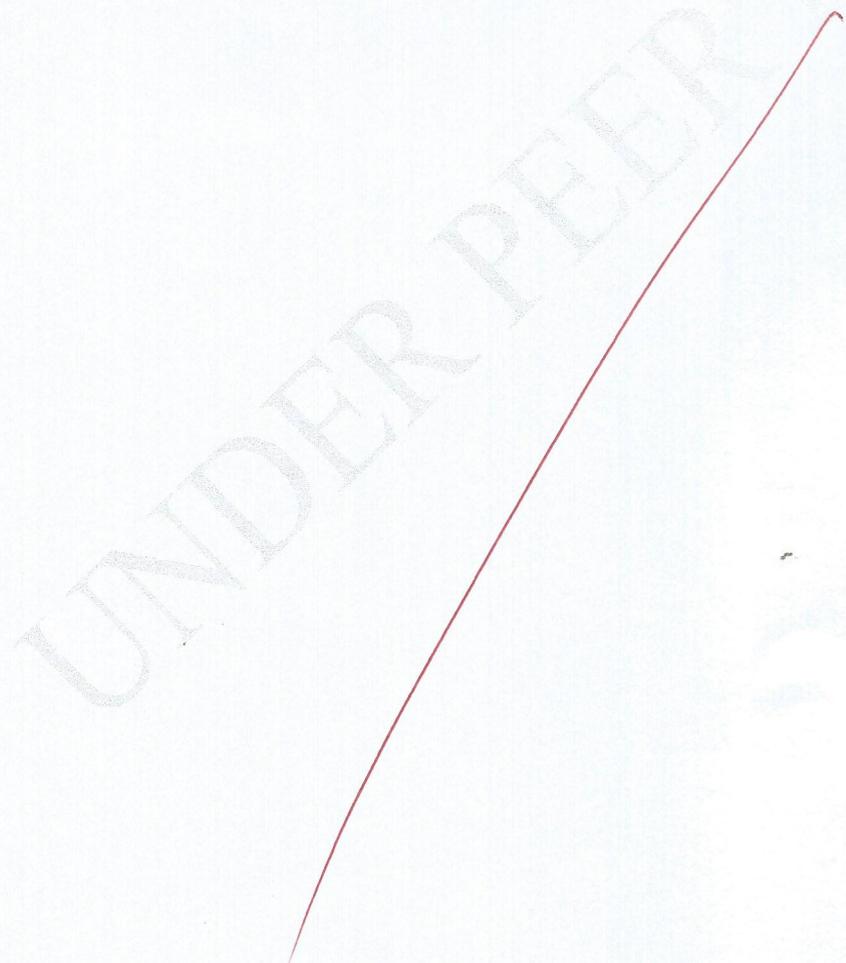
the available Fe in the soil is statistically significant as it decreases with the depth and an increase in the distance or the spatial variation.

However, the ^{con}centration of Zn ranged from 7.35ppm to 0.04ppm with an average concentration value of 34.15ppm. The high content of Zn may be attributed to the deposition of accumulated dust. In the absence of any major metal smelting operations, the primary source of Zn in urban street is probably the attrition of vehicle tire rubber. Sewage sludge soils show higher concentration of Zn and addition of fertilizers to the soil such as nitrate, phosphate and ammonium nitrate increases the concentration of Zn. The result revealed that the soil samples taken at locations A and B were highly polluted but the analyzed samples taken at location C showed that the soil samples were slightly polluted ~~but~~ by Zn. This could be attributed to the absence ^{of} minor smelting operation at ~~the~~ location C which is about 2km away from the quarry site. Cadmium, Cd was rarely observed with the highest concentration level of 1.50ppm at the topsoil layer (0-5cm) and also has a concentration value of 1.10ppm at the sub-soil layer (5-10cm) in the soil samples taken from location A. There was no detectable quantity of Cd in the analyzed soil samples from the other two locations (B and C). ^{Table 7} ~~The table~~ also shows that the concentration values of Pb in the soil samples ~~which~~ indicated that Pb was concentrated in the pollution source environment (location A) at the top soil layer (0-5cm) and sub-soil layer (5-10cm) with 4.43ppm and 3.41ppm concentration values respectively (^{Figure 1} Figure 6). It was observable that the assessment of Pb follows the same pattern as Cd with respect to the non-detectable level of contaminants in locations B and C. The concentration of Cr decreased with increase in distance to the quarry site, with the least value (0.03ppm) at location C which is 2km away from the quarry site while the highest value (5.23ppm) was observed in location A at 0-5cm depth level. It was observed that at location C, the sub-soil layers (5-10cm) and (10-25cm) indicated the absence of chromium in the soil samples analyzed and this can be attributed to the

You need to discuss figures 1 to 5 before discussing figure 6

distance to the quarry site which makes it less polluted at the top layer (0-5cm) with 0.03ppm concentration value (Figure 7).

In general, the result indicated that Fe emerged as the dominant heavy metal with a mean concentration of 148.84ppm while Cd has the lowest mean concentration of 0.29 ppm in sampled soils in all depth and spatial variations (distances). It was observed from the vicinity of quarrying area soil that the mean concentration values of the assessed heavy metals followed the sequence Fe>Zn>Cu>Cr>Mn>Pb>Cd (Figure 8). Although Pb and Cd were rarely detected as the distance increased (Figure 8), the distributions of the assessed heavy metals with their deep soil profile ranging from 0-25cm for the locations (A, B and C) are statistically illustrated as by the following graphs in Figures 1 to 7.



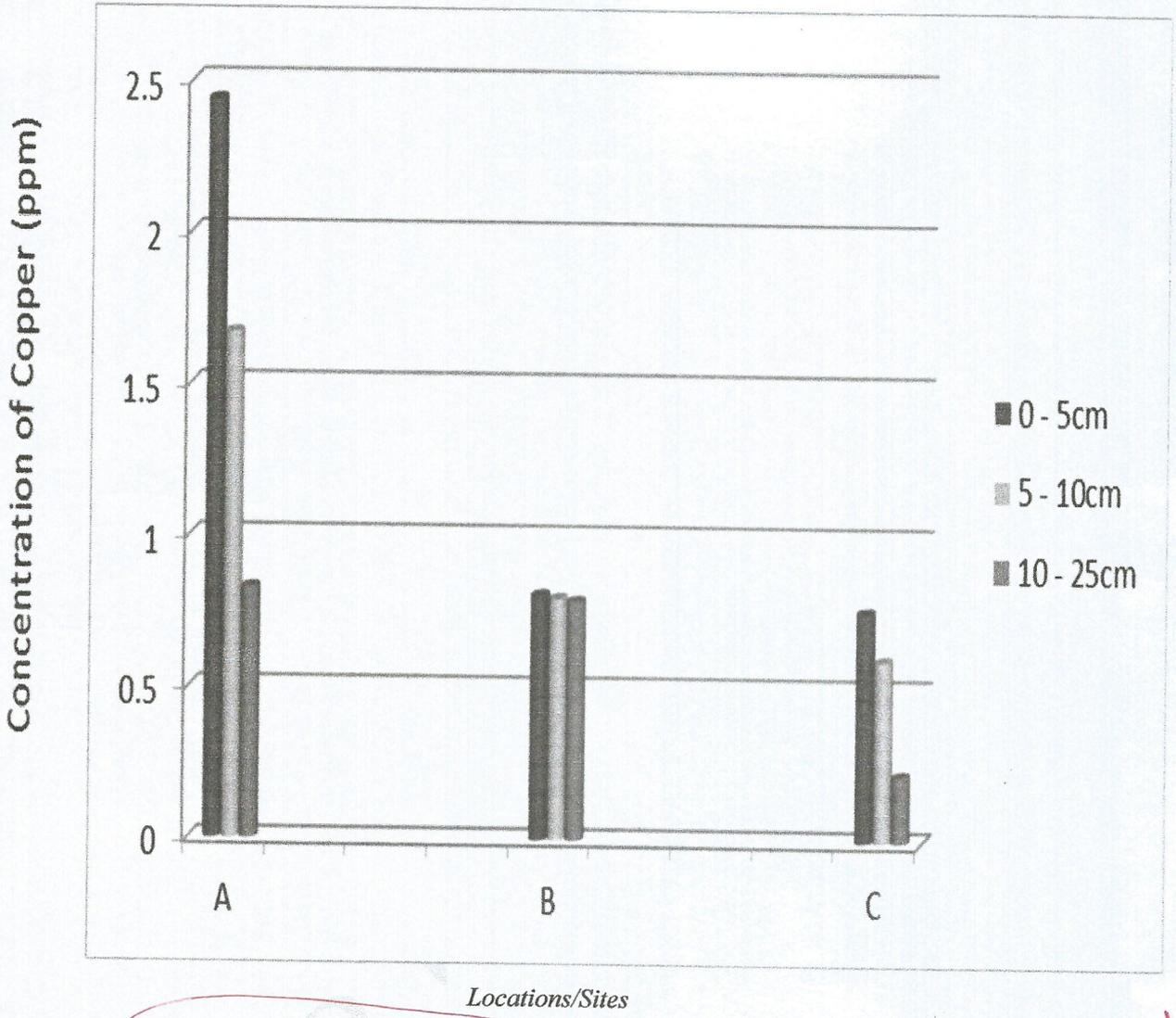


Figure 1: ~~Soil Deep Profile~~ ^{soil} for Copper Concentrations in the Samples ~~at~~ ^{at} ~~Various~~ ^{at} ~~Depth~~ ^{Various Depths}. **Bold**

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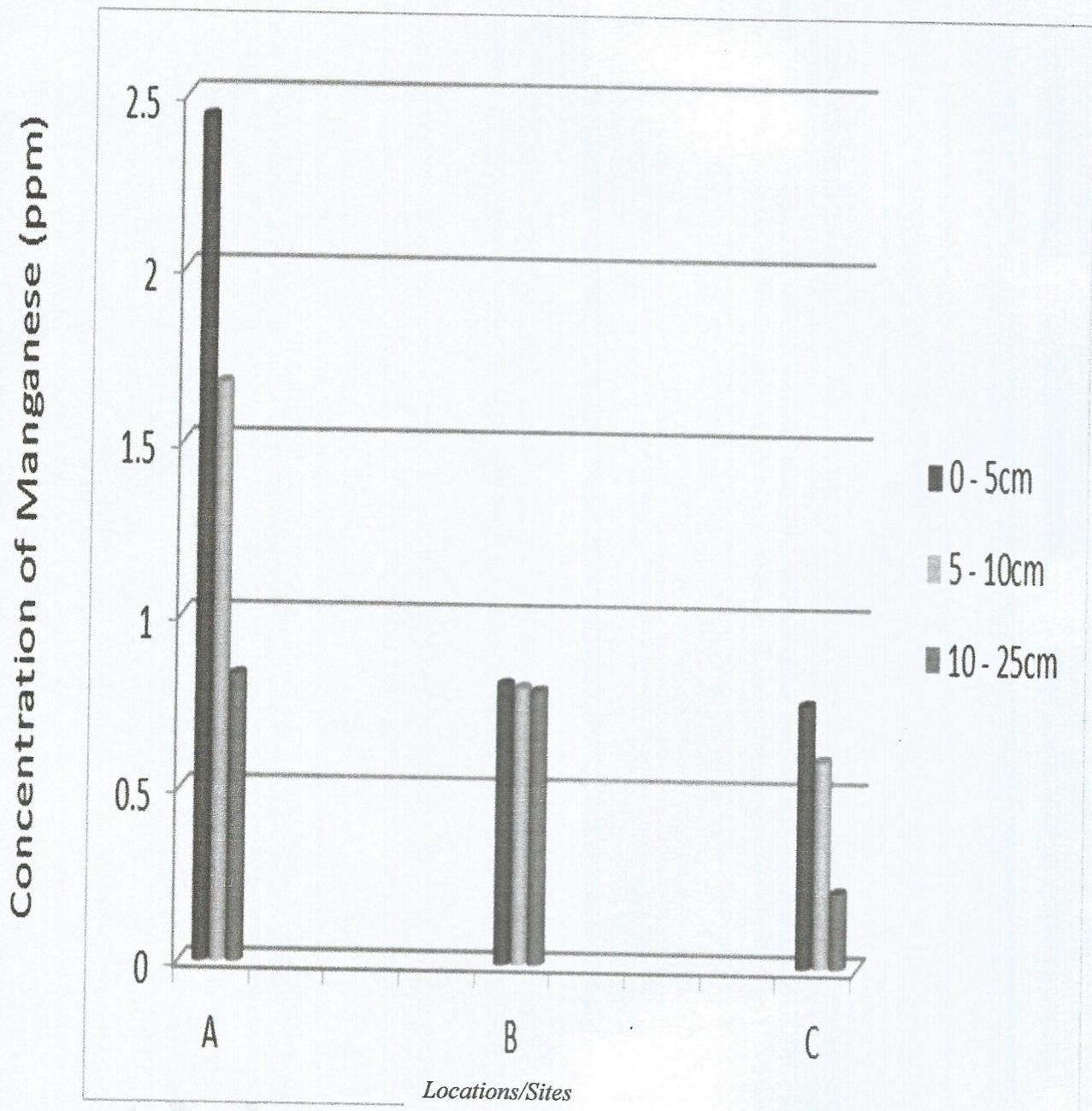


Figure 2: Soil ~~Deep~~ ^{Soil} Profile for Manganese Concentration in the Samples ^{at varying depths}

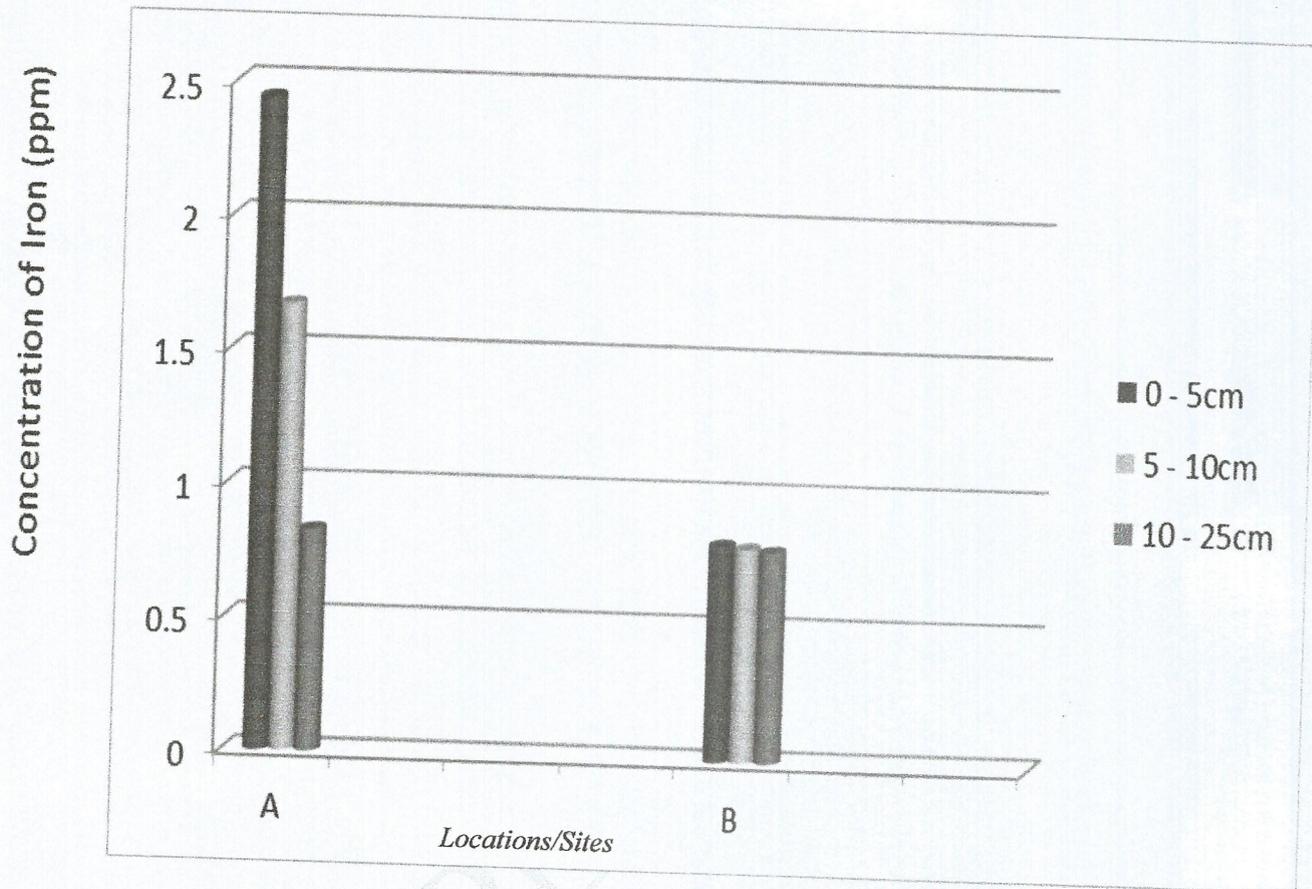


Figure 3: ~~Soil Deep Profile~~ for Iron Concentration in the ^{Soil} Samples _{at} ^{at} Varying Depths

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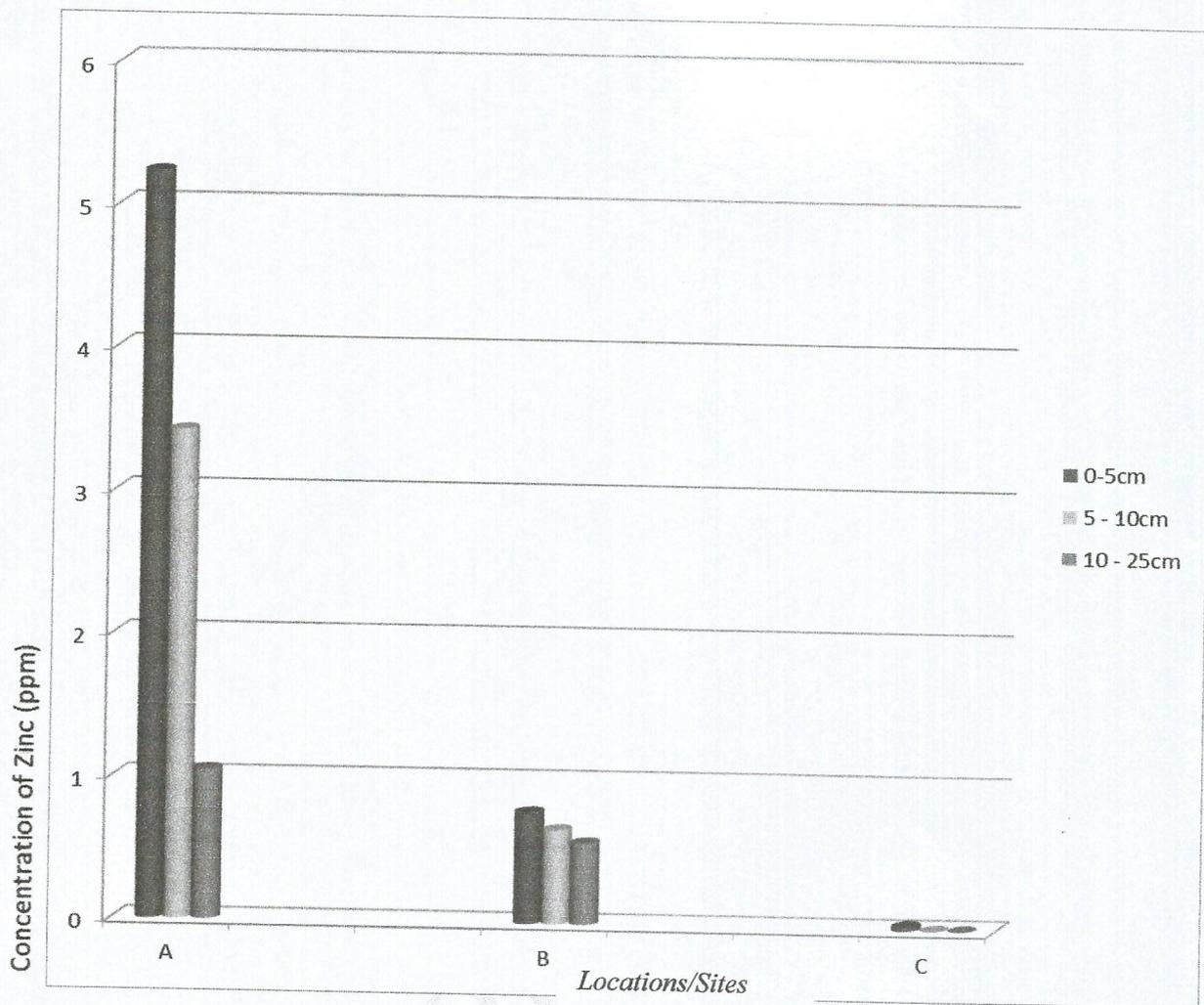
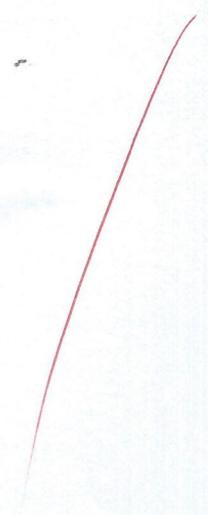


Figure 4: ~~Soil Deep Profile~~ ^{Soil} Profile for Zinc Concentration in the Samples ^{at Varying} Depths

UNDER REVIEW



Concentration of Cadmium (ppm)

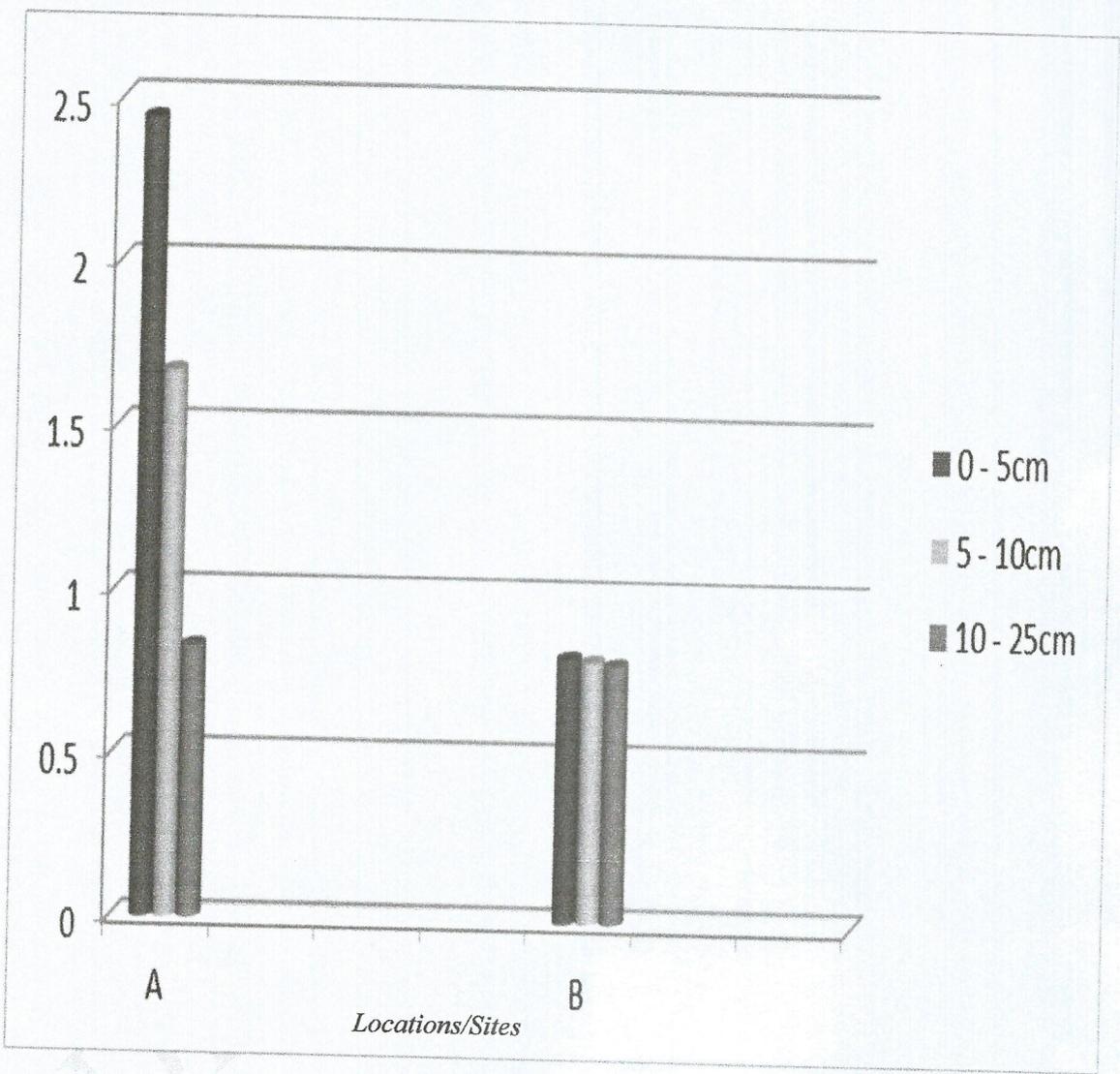


Figure 5: ~~Soil Deep Profile~~ ^{Soil} Profile for Cadmium Concentration in the ~~Samples~~ ^{at Varying} Samples ~~at Varying~~ ^{Depths} Depths



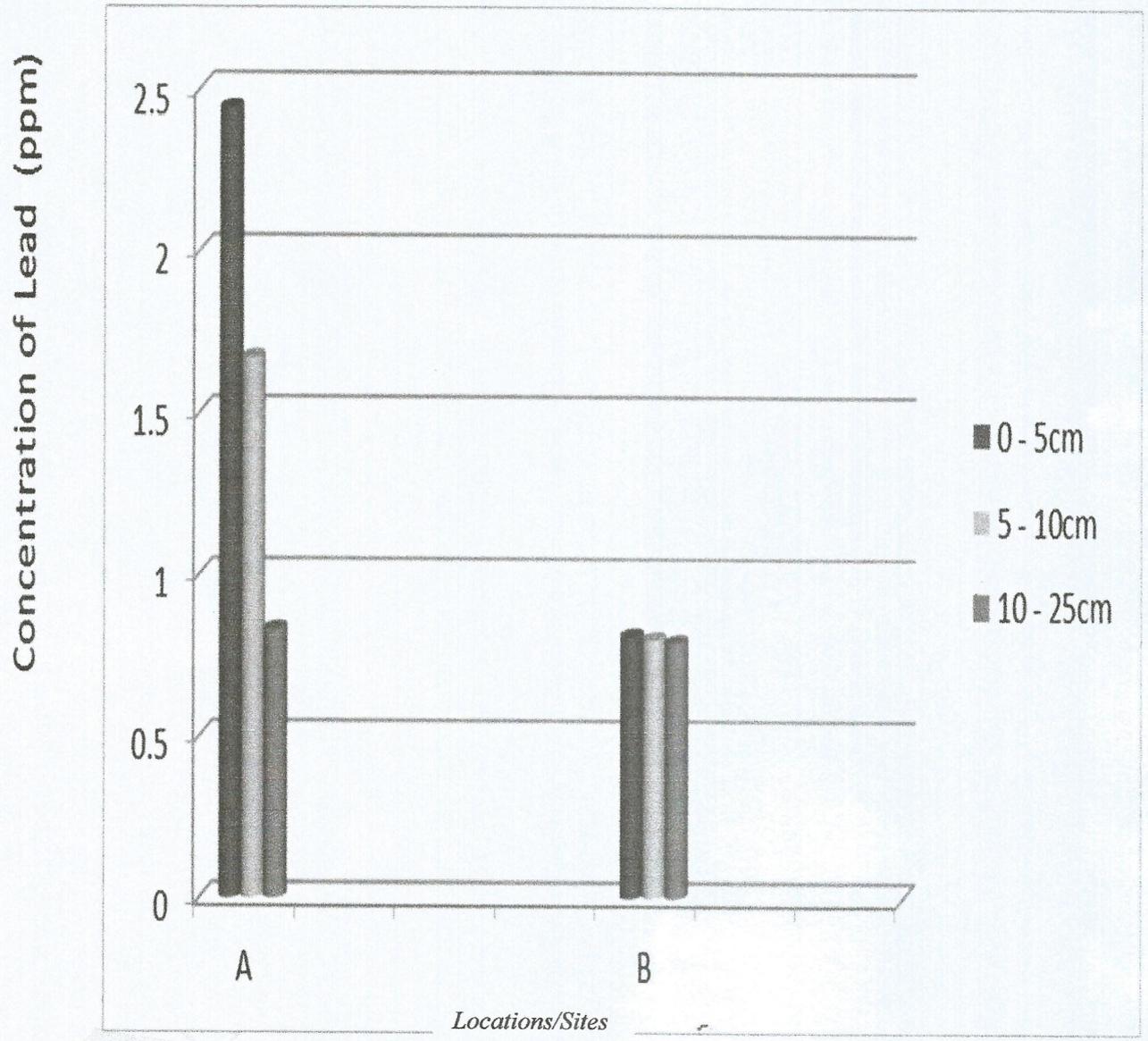


Figure 6: Soil ~~Deep Profile~~ ^{soil} for Lead Concentration in the Samples _{at} ^{at} Varying Depths



Concentration of Chromium (ppm)

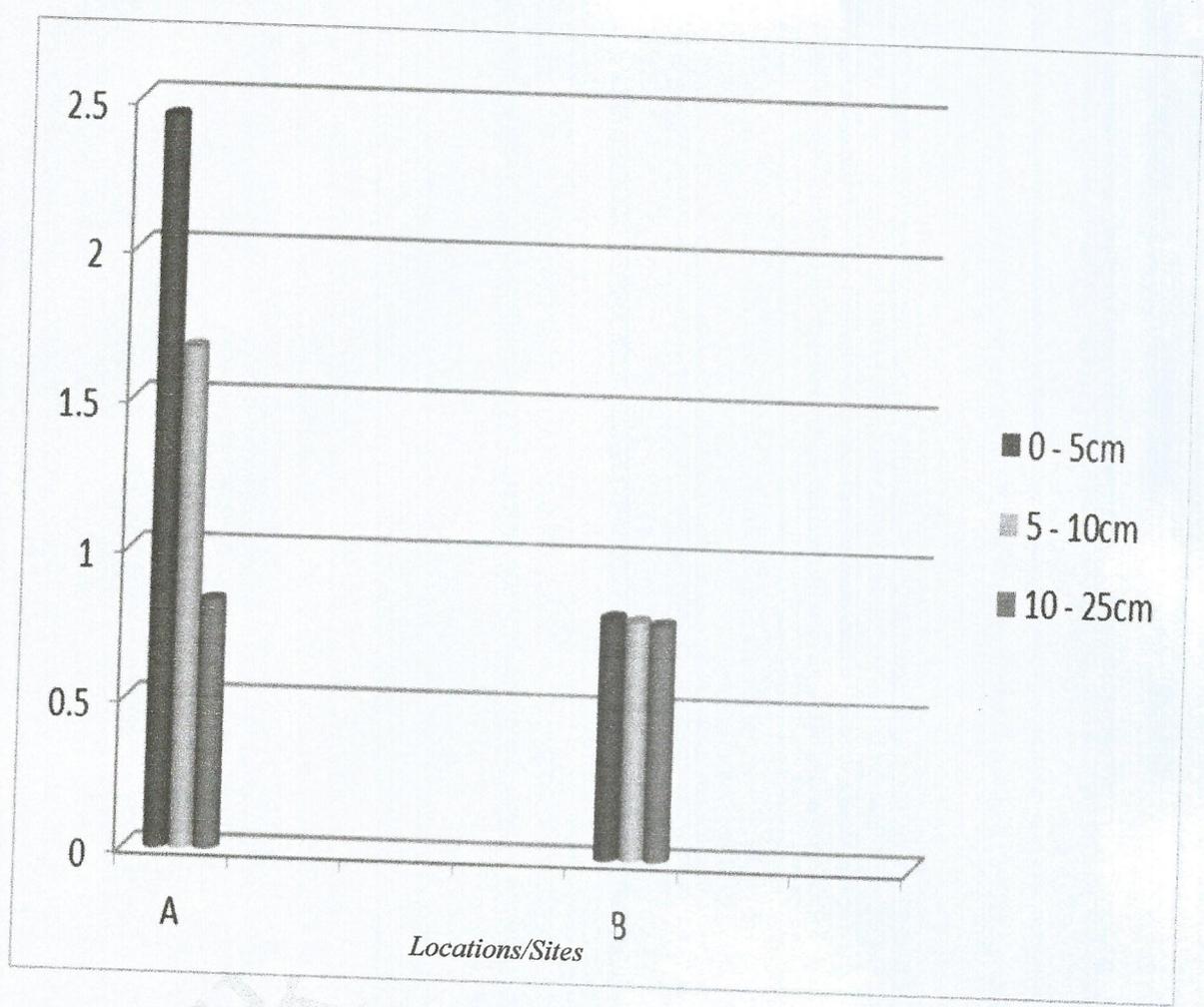


Figure 7: ~~Soil Deep Profile~~ for Chromium Concentration in the ^{Soil} Samples ₁ at Varying Depth

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Mean Concentration of Heavy Metals (ppm)

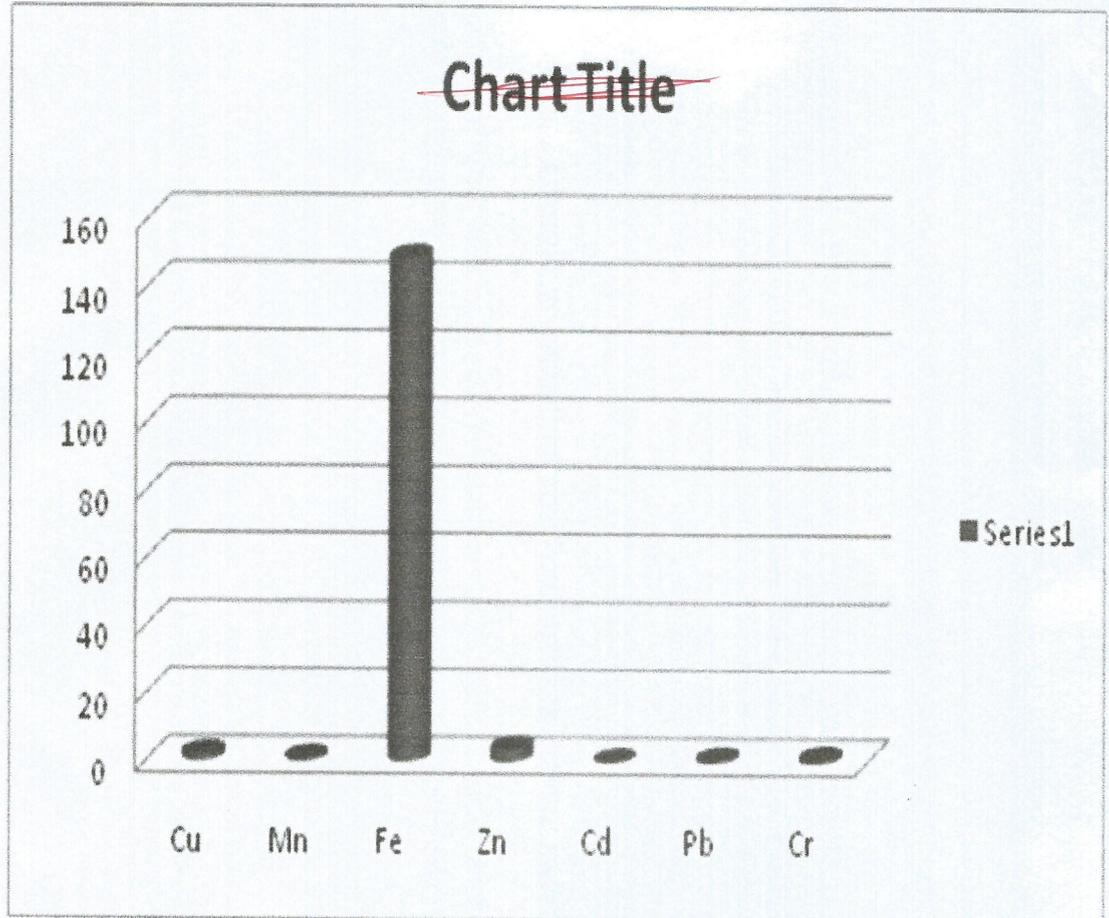


Figure 8: ~~Soil Deep Profile~~ of Heavy Metals Concentration in the Samples ^{Soil}

UNDER P...

Soil

3.2 Discussion

The assessment of the concentration of heavy metals in soils showed significant differences between samples in different distances. Results of this study showed that there was a marked decrease in concentration of Cd, Pb, Mn, Cr, Cu, Zn and Fe in soil as the sampling distance increases (Figures 1-7). The highest value of Zn (7.35ppm) observed at the topsoil layer (0-5cm) from the study site was higher than Zn (1.05ppm) recorded at the topsoil layer (0-5cm) in the soil sample 2km away from the quarry site. Soils at a distance of 300m from the quarry plant site were still contaminated, but the concentration decreased exponentially with the distance. Soil samples collected between 0km and 1km appeared to show higher concentration of most heavy metals than samples farther away probably because of their proximity to the exploration area and leaching of metals from quarry tailing. The composition of Fe, Zn, Cu, Cr, Mn sampled at various distances are ~~decreasing with large casing distance~~ ^{decreased with increase in} (Figures 1-4 and 7). ^{from the quarry site as shown in} Though Pb and Cd from the experimental analysis were infinitesimal but still follow the regular pattern of decrease in concentrations as the spatial ^{distances} ~~variation (distance)~~ increases (Figures 5 and 6). Figures 1 to 4 and Figure 7.

However, the concentration of heavy metals in soil in dry season were significantly (0.05) higher than concentration of metals in wet season. This is in agreement with the findings of [23]. This might be due to the run-off effect that is capable of removing heavy metals from the site and the effect of rainfall which may facilitate the dilution of soil solution during the wet season and intense evaporation in the dry season makes soil solution more concentrated. A ^e Concentration of heavy metals in the soil samples vary considering the topography of the area, atmospheric influence and farmland cultivation in the ^{area of the quarry site.} geographical region. //

Iron was found to be in high concentrations in most of the soil samples. This can be attributed to the soil in the investigated areas being rich in Fe. The Mn content varies from 0.22-2.44ppm. The concentration of the toxic heavy metal Cd in the results obtained from the analyzed soil samples

Did you also take samples during the dry and wet season to compare the concentration levels of the heavy metals in the soil samples to compare? Your results, presented here did not show ~~this~~ this. Otherwise, indicate the months of sampling to show data and wet.

was too low to be detected by the analytical technique used in this study as the distance from the quarry site increases. The non-detectable level of Cd in the soil samples assessed indicated that the soils around the quarry site were not contaminated with Cd.

The elemental concentration of Cr in the results of the samples assessed ^{ranged} ~~ranging~~ from 0.03-5.23ppm. The highest concentration of Cr was recorded for the topsoil sample layer (0-5cm) in the quarry site with ^a ~~concentration~~ value of 5.23 ppm ^{as shown in Figure 7.} ~~(Figure 7)~~. Lower values of Cr in soil samples in the quarry site with increase in ^{distance} ~~the spatial variation (distance)~~ were observed. Also the results obtained indicated that the concentration of Pb ranged from 3.41-4.43ppm and it was rarely detected as the ^{distance increased from the quarry site as shown in Figure 6.} ~~spatial variation (distance) increases (Figure 6)~~.

4. CONCLUSION

The assessment of the concentration of heavy metals in soils around the quarry site showed that the concentrations of heavy metals from soil samples were decreasing with increase in distance ^{from the quarry site} ~~(spatial variation)~~. It was also deduced that the concentrations of heavy metals in the soil samples decreased as the soil depth ^{increased} ~~increasingly~~ rise from 0-25cm. It was noticeable that metals like Fe, Mn, Cu, Zn and Cr were densely detected while metals like Pb and Cd were rarely detected as the distance from the quarry site significantly increased from 0-2km. This may be due to the landscape topography, soil chemical composition, regional and microclimatic effects on the study area. However, the concentrations of heavy metals in the study area was observed to be lower than the concentrations of metals in other quarrying/mining industrial sites such as the limestone quarry in southwest (Ibadan), Nigeria. This can be attributed to the number of years the quarry plant in the study area has been in operation.

From the results, the concentration of heavy metals still falls below the WHO limits but accumulation over time could be dangerous, therefore, there is ^{the} ~~is~~ need to carry out periodic Environmental Inspection Assessment studies on industrial activities and their impact on the

environment. This will prevent and minimize the negative effects of quarrying operations on human health including the factory workers and the physical environment thereby protecting the environment from hazardous pollutants.

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